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VOLUME 5 No. 5

MAY, 1954



PERGAMON PRESS LTD. LONDON

GEOCHIMICA ET COSMOCHIMICA ACTA

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VOLUME 5, No. 5

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Publishing Offices: Pergamon Press Ltd., Maxwell House, Marylebone Road, London, N.W.1 (AMB 3421).

Subscription per volume (including postage) £4 10s. (U.S.A. \$12.60).

Distributors: Lange, Maxwell & Springer Ltd., Maxwell House, Marylebone Road, London, N.W.1.
and Lange, Maxwell & Springer Inc., 122 East 55th Street, New York 22, N.Y.

PERGAMON PRESS LTD., MAXWELL HOUSE, MARYLEBONE ROAD, LONDON, N.W.1

The transport and deposition of uranium, ionium and radium in rivers, oceans and ocean sediments*

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(Received 15 December 1953)

ABSTRACT

The important factors controlling the concentration of the radioelements in the oceans are the influx, the rate of radioactive decay, and the rate at which the radioelements are removed by sedimentation. With such data as are available for the concentration of uranium and radium in ocean water, their rates of influx, and their rates of deposition, it is possible to estimate the concentration of ionium in sea water ($3.1 \pm 1 \times 10^{-15}$ gm/cc, and the amount of ionium annually transported into the oceans. It may be further concluded that in the geochemistry of uranium, influx and deposition in shallow water are of major importance while in the case of ionium, influx and deep water deposition seem most important and in the case of radium, the production by radioactive decay of ionium, the disintegration of radium itself, and deep water deposition are important factors. Ionium is not in equilibrium with uranium in ocean water.

INTRODUCTION

During the past two decades considerable data have been accumulated bearing on the subject of the concentration of uranium, ionium, and radium in ocean water and in ocean bottom sediments. It seems timely to correlate these data and to present a unified picture of the dynamics of the distribution of these elements in the oceans.

THE CONTROLLING RATE EQUATIONS

The rate of change of the uranium concentration in ocean water is determined by four processes:

- (a) The rate of radioactive decay of uranium.
- (b) The rate of removal of uranium by precipitation, co-precipitation, or absorption (and base exchange) on sediments.
- (c) The rate of influx of uranium from terrestrial sources.
- (d) The rate of influx of uranium from submarine volcanic sources.‡

The following notation is used:

U_o = concentration of uranium in ocean water (gm/cc)

λ_U = decay constant of uranium (years⁻¹)

dm/dt = rate of sedimentation (gm/year per cc of ocean water)

U_s = gm uranium removed from ocean water per gram of sediment

dv/dt = rate of influx of water into the oceans (cc/year per cc of ocean water)

U_r = concentration of uranium in river water flowing into the oceans (gm/cc)

* The work described in this paper forms part of a dissertation submitted by the senior author to the Department of Geology of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Lamont Geological Observatory Contribution No. 68.

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‡ The effect of additions from this source appear to be of local significance only.

It follows that

$$\frac{dU_o}{dt} = -\lambda_U U_o - U_s \frac{dm}{dt} + U_r \frac{dv}{dt} \quad (1)$$

For the other pertinent members of the uranium disintegration series analogous equations can be written; thus for ionium (Th^{230}), the daughter element of U^{234} ,

$$\frac{d\text{Io}_o}{dt} = -\lambda_{\text{Io}} \text{Io}_o - \text{Io}_s \frac{dm}{dt} + \text{Io}_r \frac{dv}{dt} + \lambda_U U_o \quad (2)$$

and for radium, the daughter element of ionium,

$$\frac{d\text{Ra}_o}{dt} = -\lambda_{\text{Ra}} \text{Ra}_o - \text{Ra}_s \frac{dm}{dt} + \text{Ra}_r \frac{dv}{dt} + \lambda_{\text{Io}} \text{Io}_o \quad (3)$$

The additional term in equations (2) and (3) takes into account the rate of production of ionium and radium by the radioactive decay of the respective parent element.

The problem now consists of evaluating the terms of equations (1), (2) and (3) and thus to develop a consistent interpretation of the distribution of the three radioelements in the oceans.

THE CONCENTRATION OF THE RADIOELEMENTS IN OCEAN WATER

The concentration of two of the radioelements in the oceans has been determined. HERNEGGER and KARLIK (1935) and KARLIK *et al.* (1939) have found values ranging from 0.37 to 1.28×10^{-9} gm/cc for the concentration of uranium in near shore ocean water of Skagerak and Gullmar Fjord. Later KOCZY (1950) published some additional analyses, which indicate values between 1.1×10^{-9} and 1.4×10^{-9} gm U/cc of ocean water. The considerably lower values found by RONA (1943) are ascribed by KOCZY (1950) to insufficient acidification of the samples and consequent removal of uranium on the walls of the container. The average of more recent determinations by RONA and URRY (1952) is 0.62×10^{-9} gm U/cc. The most recent published analyses by NAKANISHI (1951) indicate an average uranium concentration of 2.8×10^{-9} gm/cc in ocean water. This figure agrees well with other recent determinations and NAKANISHI's value will be used in the arguments developed below.

EVANS, KIP, and Moberg (1938) made radium determinations on U.S. Pacific coastal waters, obtaining values from 0.33 to 2.9×10^{-16} gm radium/cc. FOYN *et al.* (1939) also carried out radium measurements at the localities of their uranium analyses. The values range from 0.38 to 0.68×10^{-16} gm radium/cc. but the salinities were mostly below those of the open ocean and hence cannot be considered entirely representative. While it is difficult to decide which values to choose because of the dependence of radium content on depth, salinity, and possibly the particular water mass which was sampled, the samples of RONA and URRY (1952) seem most representative of the ocean as a whole and yield an average value of $0.31 \pm 0.05 \times 10^{-16}$ gm radium/cc which is here adopted. No measurements of the ionium concentration in ocean water have been reported to date.

THE REMOVAL OF THE RADIOELEMENTS FROM OCEAN WATER

The terms $U_s dm/dt$ in equations (1), (2), and (3) represent the sums of terms representing the removal of the radioelements by each sediment type. We therefore write

$$U_s \frac{dm}{dt} = \sum_i U_{s_i} \frac{dm_i}{dt} \quad (4a)$$

$$I_{o_s} \frac{dm}{dt} = \sum_i I_{o_{s_i}} \frac{dm_i}{dt} \quad (4b)$$

$$Ra_s \frac{dm}{dt} = \sum_i Ra_{s_i} \frac{dm_i}{dt} \quad (4c)$$

where $\frac{dm_i}{dt}$ is the rate of deposition of sediment type i in gm/year per cc of ocean water. Furthermore

$$\frac{dm_i}{dt} = f_i \frac{A}{V} \cdot \frac{dw_i}{dt} \quad (5a)$$

where $\frac{dw_i}{dt}$ = grams of sediment of type i deposited per year per cm^2 of ocean floor

f_i = fraction of ocean floor covered by sediment type i

A = area covered by ocean water (cm^2)

V = volume of ocean water (cc)

Let h be the average depth of the oceans in cm. Then

$$\frac{dm_i}{dt} = \frac{f_i}{h} \frac{dw_i}{dt} \quad (5b)$$

Values for f_i , the fraction of ocean floor covered by the various sediment types are shown in the first column of Table 1. These data have been taken from SVERDRUP, JOHNSON, and FLEMING (1946). Since fairly accurate maps are available for many oceanic areas, the values of f_i are probably in error by not more than 10%.

On the other hand there is still much uncertainty regarding the average rate of deposition of oceanic sediments. KUENEN (1950) has discussed the data available at present. The rate of deposition of shelf sediments appears to be most variable since it is affected strongly by the rate of erosion of adjacent land areas. Values as low as 2 cm/1000 years and as high as 500 cm/1000 years have been reported, so that the proposed value of 20 cm/1000 years for the average rate of deposition may be considerably in error. Since, however, both the lower limit and the upper limit quoted above appear to reflect extreme conditions, safe lower and upper limits for the average rate of deposition of shelf sediments would appear to be 5 cm/1000 years and 80 cm/1000 years respectively.

Data on the rate of deposition of hemipelagic sediments are available mainly through the work of SCHOTT (1939) and URRY (1942b, 1949, 1950.) The estimate of the former is based on the rate of accumulation of blue mud in the equatorial

Atlantic Ocean since the end of Wisconsin glaciation. The estimate of the latter is based on the rate of accumulation of glacial marine sediments in the Atlantic Ocean as measured by the ionium method of age determination. The average rate derived from the former is 1.8 cm/1000 years, that on the basis of the latter 1.5 cm/1000 years. The minima and maxima are 0.9 and 3.3 cm/1000 years for the first method and 0.2 and 5 cm/1000 years for the second. Since the average rate of accumulation of hemipelagic sediments as a whole may not be equal to the average rate of accumulation in the Atlantic Ocean, the figure 1.6 cm/1000 years quoted in Table 1 may be in error by a factor of 2 or more.

Table 1. *The rate of deposition of ocean sediments*

Type of sediment	Fraction of ocean floor covered (f_i)	Average rate of deposition					
		in 10^{-3} gm/year per cm^2			in 10^{-9} gm/year per cc of ocean water		
		min.	most prob.	max.	min.	most prob.	max.
Shelf	0.08 ± 0.01	5	20	80	0.9	4.2	19
Hemipelagic	0.18 ± 0.02	0.5	1.6	5	0.2	0.76	2.6
Pelagic	0.74 ± 0.07						
globigerina ooze	$0.35 \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} 0.36 \pm 0.04$	0.5	1.5	3.0	0.5	1.4	3.2
pteropod ooze	$0.01 \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\}$						
red clay	0.28 ± 0.03	0.2	0.6	1.5	0.13	0.45	1.2
diatom ooze	$0.08 \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} 0.10 \pm 0.01$	0.3	0.8	1.8	0.08	0.21	0.52
radiolarian ooze	$0.02 \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\}$						

Average ocean depth (h) = 3.8×10^5 cm.

The same can be said concerning the data on the rate of accumulation of globigerina ooze and pteropod ooze. SCHOTT'S (1939) average for the sedimentation rate of globigerina ooze in the Atlantic Ocean is 1.2 cm/1000 years whereas in the South Indian Ocean only 0.6 cm/1000 years appear to be deposited. URRY'S (1950) values range from 0.82 to 2.5 cm/1000 years, so that an average value of 1.5 cm/1000 years seems reasonable. This is consistent with the weighted average of all the methods of approximation given by KUENEN (1950). The limits of error are estimated to be 0.5 cm/1000 years and 3.0 cm/1000 years respectively.

SCHOTT (1939) suggests an average value of 0.54 cm/1000 years for the rate of deposition of red clay in the Indian Ocean and a value less than 0.86 cm/1000 years in the Atlantic Ocean. 0.5 cm/1000 years is the average rate indicated by the

results derived by means of the ionium method. An average value of 0.6 cm/1000 years has been adopted here. The rate of deposition of diatom ooze appears to be greater than that of red clay.

The above figures expressed the rate of accumulation uncorrected for water content. KUENEN (1950) reports that in general samples of muds and oozes contain 50% to 80% of water by volume. If an average value of 65% for the water content of ocean sediments is assumed, and if the average grain density of ocean sediments is taken to be 2.7 gm/cc, then the rate of accumulation of sediments in cm/1000 years is numerically approximately equal to the rate of accumulation in gm/1000 years of dried sediments as shown in columns 3, 4, and 5 of Table 1.

It now remains to determine U_{s_i} , Io_{s_i} , and Ra_{s_i} , the amount of uranium, ionium, and radium deposited with the various sediment types. A considerable number of determinations of the total radium content of ocean bottom sediments have been made (RUBEY, 1951; SANDERMAN and UTTERBACK, 1941; SCHOTT, 1939; URRY, 1950). Averages of these figures are reproduced in column 2 of Table 2. Since Ra_{s_i} is the amount of radium contributed by ocean water to each gram of sediment of type i , it is necessary to subtract from the figures of column 1 the amount of radium already present in the mineral grains of the sediment on entering the ocean, in order to obtain the appropriate values for column 3. The quantity thus to be subtracted can be obtained approximately from the data of PIGGOT and URRY (1938, 1941a, 1942a, 1942b, 1949, 1950) on the radium content of ocean bottom sediments older than 300,000 years. It is found that the uranium present in land-derived deep sea sediments supports about 0.6×10^{-12} gm Ra/gm irrespective of sediment type. It is quite probable in the case of rock flour that most of the uranium is still present within mineral grains on entering the ocean. The assumption that approximate radioactive equilibrium exists in the mineral grains on entering the ocean is justified. Therefore Ra_{s_i} may be estimated by subtracting 0.6×10^{-12} gm Ra/gm from the total radium content of those sediments which consist predominantly of land-derived mineral grains. In the case of sediment containing appreciable quantities of precipitates or animal remains somewhat less than 0.6×10^{-12} gm Ra/gm should be subtracted. The value 0.3×10^{-12} gm Ra/gm has been used in Table 2 in computing Ra_{s_i} for globigerina ooze and radiolarian ooze since the remains of organisms often constitute approximately 50% of the total sediment. The probable limit of error of Ra_{s_i} for each sediment type has been indicated.

Column 4 of Table 2 shows the total uranium concentration of ocean bottom sediments. The values for deep-sea material have been derived from URRY's (1942b, 1949, 1950) data. The radium content of the cores analyzed by URRY approaches a constant value with depth. On the basis of URRY's interpretation the Ra content approaches the amount which is just supported by the decay of uranium present in the sediment. Thus the uranium concentration in these sediments can be calculated approximately from the value of the radium concentration at depth in the sediment. The only direct uranium determinations available at this time are those of URRY (1941b) on three samples of globigerina ooze from a core taken in the Cayman Trough. An average value of 0.84×10^{-6} gm/gm of uranium

was found. This is in good agreement with the data on the radium content of the sediment from this core interpreted as suggested above.

The average value of the uranium content of shelf sediments is open to some question. URRY's (1949) study of a core of sediments from a shelf area indicates an average value of 1.15×10^{-12} gm/gm for the radium content of the sediment.

Table 2. Weight of uranium and radium removed from the ocean per gram of various types of sediments

Type of sediment	Total Ra content in 10^{-12} gm/gm	Ra added during sedimentation (Ra_{s_i}) in 10^{-12} gm/gm	Total U content in 10^{-6} gm/gm	U added during sedimentation (U_{s_i}) in 10^{-6} gm/gm
Shelf	0.8 ± 0.2	0.2 ± 0.3	3.0 ± 1.0	1.0 ± 0.5
Hemipelagic				
glacial marine	2.6 ± 0.4			
blue mud	3.0 ± 0.4	2.0 ± 0.5	2.5 ± 1.0	0.5 ± 0.4
Pelagic				
globigerina ooze	4.1 ± 0.6	3.8 ± 1.0	1.0 ± 0.5	0.0 ± 0.4
red clay	12.0 ± 1.5	11.5 ± 2.0	1.8 ± 0.5	0.0 ± 0.4
radiolarian ooze	13.0 ± 2.5	12.7 ± 3.0	1.0 ± 1.0	0.0 ± 0.4

No inequilibrium between radium and its parent elements ionium and uranium was indicated. If equilibrium actually did prevail, the uranium content of the sediment was on the order of 3.2×10^{-6} gm/gm. If this assumption is also valid in the case of the sediments studied by UTTERBACK and SANDERMAN (1941, 1948) off the coast of Alaska, then the uranium content of these sediments is on the order of $(1.8 \pm 0.4) \times 10^{-6}$ gm/gm.

That the average uranium content of shelf sediments is in the vicinity of 3×10^{-6} gm/gm is suggested by the results of the determination of the uranium content of marine shales (BEERS and GOODMAN, 1944). It appears that the difference between the uranium content of these shales and that of deep sea sediments is significant and is related to the removal of uranium by marine organisms. This is indicated by the relationship of the uranium and carbon content of Paleozoic shales established by BEERS and GOODMAN (1944), and a similar relationship found to exist by BURTON and SULLIVAN (1951) in Tertiary sediments.

In order to determine U_{s_i} , the quantity of uranium removed from ocean water and incorporated per gm of sediment of type i , the average uranium content of sediment entering the oceans must be known. In Table 3 the data on the uranium content of igneous and sedimentary rocks of SEFTLE and KEEVIL (1947), EVANS and GOODMAN (1941) and BELL, GOODMAN, and WHITEHEAD (1940) have been assembled together with PETTIJOHN'S (1949) figures for the relative areal extent of granitic, intermediate and basic rocks. The accuracy of the data on the uranium

content and areal extent of the various rock types is probably on the order of $\pm 10\%$. On this basis the average uranium content of rocks exposed to subaerial weathering is $(2.5 \pm 0.5) \times 10^{-6}$ gm/gm.

Table 3. Average uranium content and area covered by the more important rock types

Rock type	Average uranium content	Fraction of earth's land surface covered	(A) (B)
	(A) in 10^{-6} gm/gm	(B)	
Granitic rocks	3.96 ± 0.4	0.10 ± 0.01	0.40 ± 0.08
Intermediate rocks	2.61 ± 0.3	0.15 ± 0.01	0.39 ± 0.07
Basic rocks	0.96 ± 0.1	0.001 ± 0.001	0.00 ± 0.00
Shales	3.1 ± 0.3	0.33 ± 0.03	1.02 ± 0.20
Sandstones	2.0 ± 0.2	0.24 ± 0.02	0.48 ± 0.09
Limestones	1.3 ± 0.1	0.18 ± 0.02	0.23 ± 0.05
			Total 2.52 ± 0.49

It is to be expected that the uranium content of rock fragments carried by rivers and deposited in the oceans is equal to this value or slightly less due to the removal of uranium by leaching. Thus it appears that the uranium content of red clay $(1.8 \pm 0.4) \times 10^{-6}$ gm/gm is essentially equal to the uranium content of the constituent grains on entering the oceans, whereas the uranium content of shelf sediments has been increased, probably by the mechanism suggested above.

The weight of uranium removed from the ocean by the sediments (U_{s_i}) therefore is $(0.0 \pm 0.4) \times 10^{-6}$ gm/gm for pelagic sediments, $(1 \pm 0.5) \times 10^{-6}$ gm/gm for shelf sediments and probably of intermediate value, $(0.5 \pm 0.4) \times 10^{-6}$ gm/gm for hemipelagic sediments.

Little is known at this time about the ionium concentration in oceanic sediments. ISSAC and PICCIOTTO (1953) have reported on the ionium content of five samples taken from two cores of deep sea sediments from the Pacific Ocean. The ionium content near the surface of the cores was 14 and 20×10^{-10} gm/gm of sediment respectively. Since in deep sea sediments containing the normal value of 2×10^{-6} gm uranium/gm the ionium concentration at equilibrium is 0.3×10^{-10} gm/gm, most of the ionium present in these sediments appears to have been added during the sedimentation process. This conclusion is corroborated by an analysis of the variation of radium with depth in the cores studied by URRY. From his data the ratio of ionium to radium in cores of deep sea sediments can be calculated. The calculated values are reproduced in Table 4. The variations are considerable, but it appears probable that the ratio of ionium incorporated during the sedimentation process to radium incorporated during sedimentation is not greatly affected by sediment type. The average value of the ratio Io_{s_i}/Ra_{s_i} is 180. The quantity of excess ionium present in recently deposited red clay might thus be expected to be on the order of $180 \times 11 \times 10^{-12}$ gm/gm, i.e. 20×10^{-10} gm/gm. The agreement between this figure and the values found by ISAAC and PICCIOTTO

Table 4. Summary of URRY's core data for deep-sea sediments

Core No.	Sediment type	Lat.	Long.	Depth of water	$Ra_s \times 10^{12}$	$Io_s \times 10^{10}$	$\frac{Io_s}{Ra_s} \times 10^{-2}$
N-2	red clay	32° 21'S	105° 56'W	4217 m	8.4 ± 0.8	14.0 ± 2.0	1.7 ± 0.4
N-3	glacial marine	68° 26'S	179° 35'W	3834 m	3.1 ± 0.6	4.8 ± 0.8	1.55 ± 0.4
N-4	glacial marine	69° 12'S	179° 34'E	4345 m	1.9 ± 0.2	3.7 ± 0.7	1.95 ± 0.3
N-5	glacial marine	70° 17'S	178° 23'W	3483 m	1.1 ± 0.1	2.5 ± 0.5	2.3 ± 0.3
P-135	glob. ooze	19° 18'N	76° 48'W	4900 m		1.8 ± 0.4	
P-136	glob. ooze	18° 38'N	79° 12'W	4650 m	0.82 ± 0.1	1.5 ± 0.3	1.8 ± 0.4
P-137	glob. ooze	19° 14'N	80° 20'W	4890 m	0.90 ± 0.1	1.7 ± 0.3	1.9 ± 0.3
						Average	1.8 ± 0.2

(1953) is probably partially fortuitous since in their samples the ratio Io_{si}/Ra_{si} was 50 rather than 180. No conclusive data for this ratio in near shore sediments are available.

THE RATE EQUATION FOR URANIUM

It is now possible to derive the value of the various terms of equation (1). The best value for the average uranium concentration in the oceans was stated to be $(2.8 \pm 1.0) \times 10^{-9}$ gm/cc; λ_U is $(1.52 \pm 0.01) \times 10^{-10}$ years⁻¹. Therefore $\lambda_U U_o$ the quantity of uranium subtracted per cc of ocean water per year by radioactive decay is $(3.5 \pm 1.5) \times 10^{-19}$ gm/year per cc of ocean water.

In Table 5 the values of the rate of removal of uranium with the various sediment types have been summarized. There is a large range of possible values for the total rate of removal of uranium from the ocean, $U_s \frac{dm}{dt}$. However, even the smallest possible value of this function, 0.4×10^{-15} gm/year per cc of ocean water is much larger than the rate of radioactive decay of uranium in the oceans.

It can furthermore be shown that any rate of change of the uranium content of seawater, dU_o/dt , is probably small compared to the rate of removal of uranium with ocean sediments, $U_s dm/dt$. As has been indicated above, uranium is extracted from ocean water on the continental shelves. If the uranium concentration of ocean water in the past had been greatly different from the present value, it is to be expected that the rate of removal of uranium on the continental shelves would also have been different at this time. However BEERS' and GOODMAN'S (1944) study does not indicate a ratio of uranium to carbon in Paleozoic shales at variance with that observed in recent sediments. It is therefore probable that the uranium concentration of ocean water has not changed greatly since Paleozoic time. Furthermore very cogent reasons for the narrow limits of the chemical composition of ocean water in the past have been given by RUBEY (1951). Thus a change of 20% in the uranium concentration of ocean water during the past 10^7 years is a

conservative upper limit in calculating the rate of change of the uranium concentration in sea water (U_o). Since U_o is $(2.8 \pm 1.0) \times 10^{-9}$ gm/cc at present, rate of change of the uranium concentration in the ocean would be

$$\frac{dU_o}{dt} < \frac{0.2 \times 2.8 \times 10^{-9}}{10^7} = 0.56 \times 10^{-16} \text{ gm/year per cc of ocean water.}$$

The maximum value of the rate of change of the uranium concentration (dU_o/dt) is therefore negligible compared to the rate of removal of uranium with sediments,

$$U_s \frac{dm}{dt}.$$

Since both the loss of uranium in the ocean due to the rate of radioactive decay, $\lambda_U U_o$, and the rate of change of the uranium concentration, $\frac{dU_o}{dt}$, are small compared to the rate of removal of uranium with the sediments, $U_s \frac{dm}{dt}$, equation (1) can be written

$$0 = -U_s \frac{dm}{dt} + U_r \frac{dv}{dt} \quad (6)$$

This indicates that the rate of influx of uranium from rivers is balanced by the rate of deposition of uranium, primarily in the continental shelf areas.

According to CLARKE (1924) the volume of water annually discharged through rivers to the oceans is 2.74×10^{19} cc. The volume of the oceans has been computed (UTTERBACK and SANDERMAN, 1948) to be 1.37×10^{24} cc. The possible error in both of these determinations is probably about 10%. Thus the rate of influx of river water into the ocean is given by:

$$\frac{dv}{dt} = \frac{2.74 \times 10^{19}}{1.37 \times 10^{24}} = (2.0 \pm 0.4) \times 10^{-5} \text{ cc/year per cc of ocean water.}$$

From equation (6) and Table 5 it follows that the most probable average uranium concentration in river waters is given by:

$$U_r = \frac{U_s \frac{dm}{dt}}{dv/dt} = 2.3 \times 10^{-10} \text{ gm/cc.} \quad (6a)$$

Due to the uncertainty of the quantity of uranium deposited annually with ocean sediments the minimum and maximum values derived by this method are 2×10^{-11} and 2×10^{-9} gm/cc respectively. Direct determinations of the uranium content of river waters have been reported by RONA and URRY (1952), ADAMS, J. (personal communication, November 1953), and HOFFMANN (1942). RONA and URRY found the uranium concentration of water from the Hudson, St. Lawrence, and Mississippi Rivers to be 0.22, 0.16, and 0.40×10^{-10} gm/cc. In the light of more recent work these figures may be too low by a factor of three. ADAMS has studied river water from various parts of the United States, and has found the concentration of uranium present in true solution to be about 1×10^{-10} gm/cc. He has also found that a considerable quantity of uranium is lightly held on the surface of

suspended grains, the average uranium concentration of river water acidulated prior to filtration being 6×10^{-10} gm/cc. Other recent unpublished analyses agree with these figures.

Table 5. The rate of removal of uranium from ocean water by sediments in 10^{-15} gm uranium/year per cc of ocean water

<i>Sediment type</i>	<i>Min.</i>	<i>Most prob.</i>	<i>Max.</i>
Shelf	0.4	4.2	38.0
Hemipelagic	0.0	0.4	2.6
Pelagic glob. ooze pteropod ooze	0.0	0.0	1.2
red clay	0.0	0.0	0.5
diatom ooze radiol. ooze	0.0	0.0	0.2
<i>Total rate of removal</i> $\left(U_s \frac{dm}{dt} \right)$	0.4	4.6	42.5

These data suggest that at least some of the uranium in shelf sediments is accumulated during transportation to the ocean rather than during sedimentation in the ocean. It can be readily seen that this does not affect the applicability of equation (1) provided that U_r is defined as including the uranium carried along on the surface of suspended mineral grains.

HOFFMANN has determined the uranium concentration in the water and suspended sediment of several central European rivers. A range of values from 1.6 to 470×10^{-10} gm/cc was found for the concentration of uranium in solution. It was not stated whether the water was acidulated prior to filtration, so that it is not clear whether the reported values represent the concentration of uranium in true solution only or whether they also include the uranium held on the surface of mineral grains. On the basis of the data of RONA and URRY, ADAMS, and HOFFMANN it can be concluded that the concentration of total available uranium in rivers is close to the value found with the use of equation (6a).

Another indication of the average uranium concentration in river water can be obtained from a study of the average composition of rocks exposed to weathering. Column 2 of Table 6 shows the average concentration of Si, Al, Fe, Ca, Na, K, and Mg in rocks exposed to weathering as calculated from the data assembled by RANKAMA and SAHAMA (1950) and the areal extent of the various rock types as proposed by PETTIJOHN (1949) and DALY (1933). In column 3 data taken from RANKAMA and SAHAMA (1950) on the average concentration of these elements in

Table 6. The concentration of the common rock forming elements in river water and in rocks exposed to weathering

Element	(A)	(B)	$\frac{(B)}{(A)}$
	Average concentration in rocks exposed to weathering in 10^{-2} gm/gm	Average concentration in river water in 10^{-6} gm/gm	
Si	25.4 ± 3.0	17.1 ± 2.0	0.67 ± 0.15
Al	5.45 ± 0.5		
Fe	3.14 ± 0.3	4.0 ± 0.4	0.47 ± 0.10
Ca	8.04 ± 0.8	29.6 ± 3.0	3.7 ± 1.0
Na	1.12 ± 0.1	3.8 ± 0.4	3.4 ± 1.0
K	1.86 ± 0.2	2.9 ± 0.3	1.6 ± 0.3
Mg	2.04 ± 0.2	4.4 ± 0.4	2.2 ± 0.4

Table 7. The magnitude of the terms of equation 1 in 10^{-15} gm/year per cc of ocean water

Term	Symbol	Min.	Magnitude most probable	Max.	Source of data
Rate of radioactive decay of uranium	$\lambda_U U_o$	0.0	0.0	0.0	Direct determination of the concentration of uranium in ocean water and of the rate of radioactive decay of uranium
Rate of change of uranium concentration in the ocean	$\frac{dU_o}{dt}$	0.0	0.0	0.0	Radioactivity of shales of various ages
Rate of removal of uranium with ocean sediments	$U_s \frac{dm}{dt}$	0.4	4.6	43	Rate of deposition of ocean sediments; uranium content of marine sediments
Rate of influx of uranium in rivers	$U_r \frac{dv}{dt}$	0.4	4.6	43	Equation (1) using the above value for $\lambda_U U_o$, dU_o/dt and $U_s dm/dt$
		0.3	12	1100	Direct determinations of the uranium content of river water
		1.4		26	Relative solubility of uranium and common rock forming elements

river water is presented, and column 4 shows the ratio of the concentration in river water to the concentration in the rocks exposed to weathering. As is to be expected, the value of this ratio is smallest for Si, Al, and Fe which tend to remain in soils. It is interesting that the ratio differs only by a factor of two for the other elements considered. It is not possible to calculate the ratio $(B)/(A)$ for uranium on the basis of these data. However it is probable that the numerical value of the ratio for uranium is not less than that for Fe, Al, and Si and not greater than that for Ca, since much of the uranium in rocks occurs as an accessory element in silicate minerals. Even in the case of primary uranium oxide minerals uranium may not be removed at a more rapid rate than that with which Ca is removed from feldspar, since some of the uranium liberated from the primary uranium minerals is precipitated as secondary minerals in the immediate neighbourhood of the source. On this basis probable minimum and maximum values for the average concentration of uranium in river waters (U_r) become

$$U_r > 0.47 \times 10^{-4} \times 2.0 \times 10^{-6} = 0.9 \times 10^{-10} \text{ gm/cc}$$

$$U_r < 3.7 \times 10^{-4} \times 3.0 \times 10^{-6} = 11 \times 10^{-10} \text{ gm/cc}$$

The agreement of the minimum and maximum values calculated in this manner with the direct determinations cited above is encouraging.

THE RATE EQUATION FOR RADIUM

As was stated above, Ra_o , the average concentration of radium in ocean water is $(0.31 \pm 0.05) \times 10^{-16}$ gm/cc. If we take the decay constant to be 4.33×10^{-4} years⁻¹, the term $\lambda_{Ra} Ra_o$ in equation (3) becomes $(1.3 \pm 0.2) \times 10^{-20}$.

Considering the data on uranium previously discussed, we conclude that a 20% change of the Ra concentration would represent the maximum probable change in 10⁷ years. The rate of change of radium concentration in the ocean water, dRa_o/dt , is therefore less than

$$\frac{dRa_o}{dt} < \frac{0.2 \times 0.3 \times 10^{-16}}{10^7} = 0.6 \times 10^{-24} \text{ gm/year per cc of ocean water}$$

and is thus negligibly small compared to $\lambda_{Ra} Ra_o$. This would still be the case even if a 20% change in the Ra concentration were found to have taken place within the past 10⁵ years.

The rate of removal of radium with ocean sediments can be calculated on the basis of the values of the radium present in sediments in excess of that required for equilibrium with uranium (Ra_{s_i}) and the rate for sedimentation of the various sediment types dm_i/dt . The pertinent data are summarized in Table 8. From this compilation it follows that the most probable value of the rate of removal of radium with ocean sediments is 1.5×10^{-20} , the minimum value 0.4×10^{-20} and the maximum value 5.4×10^{-20} gm/year per cc of ocean water.

There is still much uncertainty regarding the concentration of radium in river water. As in the case of the determinations of the uranium content of river water, there is a large amount of scatter in the observed values. RONA and URRY (1952) have made measurements on water from the Hudson and St. Lawrence rivers

in North America and obtained values of 0.33 ± 0.04 and $0.25 \pm 0.04 \times 10^{-16}$ gm/cc respectively. JACOBI (1949) obtained radium values which ranged from 0.06 to 1.7×10^{-16} gm/cc for various rivers in the southern part of Great Britain. Most of the samples were found to contain $0.45 \pm 0.1 \times 10^{-16}$ gm/cc.

These variations are probably not due to errors in the experimental procedure. While the rocks over which these rivers pass contain average concentrations of

Table 8. The rate of removal of radium from ocean waters by sediments in 10^{-21} gm radium/year per cc of ocean water

<i>Sediment type</i>	<i>Min.</i>	<i>Most prob.</i>	<i>Max.</i>
Shelf	0.1	0.4	7.6
Hemipelagic	0.3	1.5	6.5
Pelagic			
glob. ooze	1.4	5.3	15.4
pteropod ooze			
red clay	1.2	5.2	16.2
diatom ooze			
radiol. ooze	0.7	2.6	8.1
<i>Total rate of removal</i> $\left(Ra_s \frac{dm}{dt} \right)$	3.7	15.0	53.8

uranium and therefore of radium, the effect of climate on the rate of solution of radium cannot be readily assessed. However, since the average content of dissolved substances in river water usually does not vary by more than a factor of two (SCHOTT, 1939), some credence may be given to the use of an average based on the above data for a world-wide value. The value $(0.35 \pm 0.10) \times 10^{-16}$ gm/cc will therefore be tentatively accepted.

As in the case of uranium an approximate value for the concentration of radium in river water can be obtained from the relative areal distribution and solubility of radium. From the data of Table 4 it follows that the average radium concentration in rocks exposed to weathering is

$$(2.5 \pm 0.5) \times 10^{-6} \times \frac{\lambda U}{\lambda Ra} = (0.9 \pm 0.2) \times 10^{-12} \text{ gm/gm.}$$

By applying the same reasoning as in the case of uranium, we can say that

$$Ra_r > 0.47 \times 10^{-4} \times 0.7 \times 10^{-12} = 0.3 \times 10^{-16}$$

$$Ra_r < 3.7 \times 10^{-4} \times 1.1 \times 10^{-12} = 4.1 \times 10^{-16}$$

This range overlaps the experimental average, confirming the order of magnitude.

In equation 3 only the value of the term $\lambda_{\text{Io}}\text{Io}_0$ representing the rate of production of radium in the oceans by the radioactive decay of ionium remains unknown, and can thus be determined. Table 9 is a summary of the data bearing

Table 9. The magnitude of the terms of equation (3) in 10^{-20} gm/year per cc of ocean water

Term	Symbol	Min.	Magnitude most probable	Max.	Source of data
Rate of radioactive decay of radium	$\lambda_{\text{Ra}} \text{Ra}_0$	1.1	1.3	1.5	Direct determination of the radium concentration of ocean water and of the rate of radioactive decay of radium
Rate of change of radium concentration	$\frac{d}{dt} \text{Ra}_0$	0.0	0.0	0.0	Probable uniformity of uranium and ionium concentration in the oceans
Rate of removal of radium with ocean sediments	$\text{Ra}_s \frac{dm}{dt}$	0.4	1.5	5.4	Rate of deposition of ocean sediments; radium content of marine sediments
Rate of influx of radium in rivers	$\text{Ra}_r \frac{dv}{dt}$	0.01	0.07	0.34	Direct measurements by RONA and URRY and by JACOBI
		0.06	—	0.8	Relative abundance of the elements and their relative rates of solution
Rate of the production of radium by the decay of ionium	$\lambda_{\text{Io}}\text{Io}_0$	1.5	2.7	6.1	Equation (3)

on the individual terms of equation (3). From these it can be seen that the maximum, most probable, and minimum values of the rate of production of radium from the radioactive decay of ionium, $\lambda_{\text{Io}}\text{Io}_0$, are 6.1×10^{-20} , 2.7×10^{-20} and 1.5×10^{-20} respectively. The decay constant of ionium is $8.6 \pm 0.1 \times 10^{-6}$ year⁻¹. Thus the maximum, most probable, and minimum values of the ionium concentration in the oceans are 7.1×10^{-15} , 3.1×10^{-15} and 1.7×10^{-15} gm/cc respectively.

By a similar approach, RONA and URRY (1952) have also calculated the average ionium content of ocean water and find it to be 3.9×10^{-15} gm/cc in satisfactory agreement with the above result.

It is of interest that the economy of radium depends mainly on the balance between the rate of production of this element by the radioactive disintegration of ionium, the radioactive decay of radium itself, and the deposition of radium with pelagic sediments. The contribution to the radium content of the oceans by influx with river water is negligible.

THE RATE EQUATION FOR IONIUM

The value derived above for the rate of radioactive disintegration of ionium in the ocean $\lambda_{\text{Io}} \text{Io}_o$ can now be introduced into equation (2) descriptive of the economy of ionium in the oceans. As in the case of radium it is probable that the change during the past 10^7 years in the ionium concentration of ocean water has been less than 20% of the present concentration. Thus the rate of change of the ionium

concentrations in ocean water, $\frac{d\text{Io}}{dt}$, is less than

$$\frac{d\text{Io}_o}{dt} < \frac{0.2 \times 3.1 \times 10^{-15}}{10^7} = 0.6 \times 10^{-22} \text{ gm/year per cc of ocean water.}$$

The value of the term $\lambda_{\text{U}} \text{U}_o$, the rate of radioactive decay of uranium in ocean waters, has already been discussed and was found to be $(3.5 \pm 1.5) \times 10^{-19}$. It therefore follows that

$$-\text{Io}_r \frac{dv}{dt} + \text{Io}_s \frac{dm}{dt} = 3.2 \pm 1.2 \times 10^{-19}$$

It should be possible to derive an approximate value for the term $\text{Io}_s \frac{dm}{dt}$, the rate of removal of ionium with ocean sediments, by means of the rate of sedimentation data of Table 1 and the value 180 for the ratio of added ionium to the added radium, Io_s/Ra_s , in deep sea sediments derived from URRY's data on the rate of variation of the radium content with depth in cores of ocean sediments. Table 10 summarizes the individual terms $\text{Io}_{s_i} \frac{dm_i}{dt}$ for the various sediment types. Thus the maximum, most probable and minimum values of the rate of influx of ionium into the ocean with river water $\text{Io}_r \frac{dv}{dt}$ are 97×10^{-19} , 28×10^{-19} , and 7.3×10^{-19} gm/year per cc of ocean water respectively.

Since the rate of discharge of river water into the ocean, dv/dt , is $(2 \pm 0.4) \times 10^{-5}$ cc/year per cc of ocean water, the maximum, most probable and minimum values of Io_r , the concentration of ionium in river water, as calculated by this method are 59×10^{-14} , 12×10^{-14} , and 0.9×10^{-14} gm/cc respectively.

These concentrations are considerably in excess of those to be expected on the basis of relative abundance measurements. The average ionium content of rocks exposed to weathering should be approximately

$$(2.5 \pm 0.5) \times 10^{-6} \frac{\lambda_{\text{U}}}{\lambda_{\text{Io}}} = (4.5 \pm 0.9) \times 10^{-11} \text{ gm/gm}$$

Furthermore if the rate of solution of ionium is less than that of calcium and greater than that of iron and aluminium

$$\text{Io}_r > 0.47 \times 10^{-4} \times 3.6 \times 10^{-11} = 0.17 \times 10^{-14} \text{ gm/cc}$$

$$\text{Io}_r < 3.7 \times 10^{-4} \times 5.4 \times 10^{-11} = 2.0 \times 10^{-14} \text{ gm/cc}$$

The source of the discrepancy between these values and those calculated above

by means of equation (2) is not at once apparent. The most likely sources of error at this time appear to be the values of I_{o_s} , the quantity of ionium removed from ocean water per gram of sediment. A check on this observation should be available when more ionium determinations have been made with the method recently developed by ISAAC and PICCIOTTO (1953).

CONCLUSIONS

The rate equations descriptive of the economy of uranium, ionium, and radium in the oceans and in ocean sediments have been developed, and the magnitude of the terms calculated by means of the experimental data available at present. The following conclusions appear to be warranted at this time.

Table 10. The removal of ionium from ocean water by sediments in 10^{-19} gm/year per cc of ocean water

<i>Sediment type</i>	<i>Min.</i>	<i>Most prob.</i>	<i>Max.</i>
Shelf	0.0	0.8	13
Hemipelagic	0.5	2.7	11
Pelagic			
glob. ooze	2.5	9.6	28
pteropod ooze			
red clay	2.2	9.3	29
diatom ooze			
radiol. ooze	1.4	4.8	15
<i>Total rate of removal</i> $\left(I_{o_s} \frac{dm}{dt} \right)$	6.6	27.2	96

1. In the case of uranium, the rate of influx and the rate of deposition with shelf sediments are nearly equal and far exceed the rate of radioactive disintegration of uranium and the rate of deposition of uranium with pelagic sediments.

2. The rate of production of radium by radioactive decay of ionium is in excess of the rate of influx from rivers. The rate of radioactive decay and the rate of deposition with pelagic sediments are also large and overshadow the rate of deposition on the shelf area.

3. In the case of ionium the rate of influx and the rate of deposition with pelagic sediments are nearly equal and appear to be greatly in excess of the rate of radioactive production and of the rate of deposition with shelf sediments. The average concentration of ionium in ocean water is $(3.1 \pm 1) \times 10^{-15}$ gm/cc.

4. More experimental data on the radium, ionium, and uranium content of river and ocean water, the rates of deposition, and the uranium, ionium, and radium content of ocean sediments are needed before a completely quantitative understanding of the economy of these elements in the ocean can be reached.

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The mechanism of removal of ionium and radium from the oceans*

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(Received 21 January 1954)

ABSTRACT

By the use of radiothorium (Th^{228}) and thorium X (Ra^{224}) as tracers for ionium (Th^{230}) and radium (Ra^{226}) respectively, it has been possible to study the adsorption and base exchange of these elements on deep-sea sediments. Extrapolation of the adsorption data obtained with these tracers to the region of the actual concentration of ionium and radium in sea water shows that the quantity of ionium and radium adsorbed is comparable to that observed on recent deep-sea sediments. This seems to demonstrate that base exchange is the mechanism by which ionium and radium are removed from ocean water. In turn this establishes the interpretation of the radium vs. depth curves as reflecting ionium decay which is the basis for the Ionium Method of age determination. Finally, this information delimits the variables which must be controlled in applying this method to the dating of events on the ocean floor.

INTRODUCTION

It has been known for some time that in sediments recently deposited on the ocean floor radium is present in amounts exceeding the quantity in equilibrium with uranium present in these sediments. PIGGOT and URRY (1941) have shown that the excess of radium is to be ascribed to the removal of this element from sea water. That ionium (Th^{230}), the parent of radium, is apparently also concentrated in ocean bottom sediments was suggested by URRY (PIGGOT and URRY, 1941; URRY and PIGGOT, 1942; 1949), and has been demonstrated recently by ISSAC and PICCIOTTO (1953). The present research was undertaken to investigate the role of base exchange in the selective removal of radium and ionium from ocean water by ocean sediments. The base exchange of radium and ionium on ocean bottom sediments was studied by determining the behaviour of ThX (Ra^{224}) and RaTh (Th^{228}) in artificial suspensions of ocean bottom sediments in sea water.

I. EXPERIMENTAL MATERIALS AND PROCEDURE

The sediment suspensions

Samples of red clay, globigerina ooze, and green clay were obtained from materials collected by Prof. M. EWING on recent trips of the Atlantis. The geographic location and depth of water at which the samples were taken are shown in Table 1 and the map of Fig. 1.

All samples except RC-1 were still wet when received at the laboratory. Sea water obtained by the Woods Hole Oceanographic Institution off-shore from Woods Hole was passed through hardened filter paper and was added to a portion of the sediment which was then dispersed by vigorous stirring. The fraction of the sediment which settled in less than 30 seconds was separated, and the volume of the remaining suspension brought up to 1000 cc with additional filtered sea water. To determine the concentration of sediment in the suspension, aliquots of the suspension were centrifuged for five minutes at 2500 rpm, and the supernatant liquid decanted. Distilled water was then added to the sediment and the process repeated, after which the sediment was transferred to a weighing bottle and dried to constant weight at 150°C. The concentration of sediment in the suspensions varied between 1.07 and 3.64 mg/cc.

* Lamont Geological Observatory Contribution No. 108. The research reported in this paper forms part of a dissertation submitted by H. D. HOLLAND to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The authors wish to acknowledge the support of the Office of Naval Research and the A. H. Phillips Fund in this investigation.

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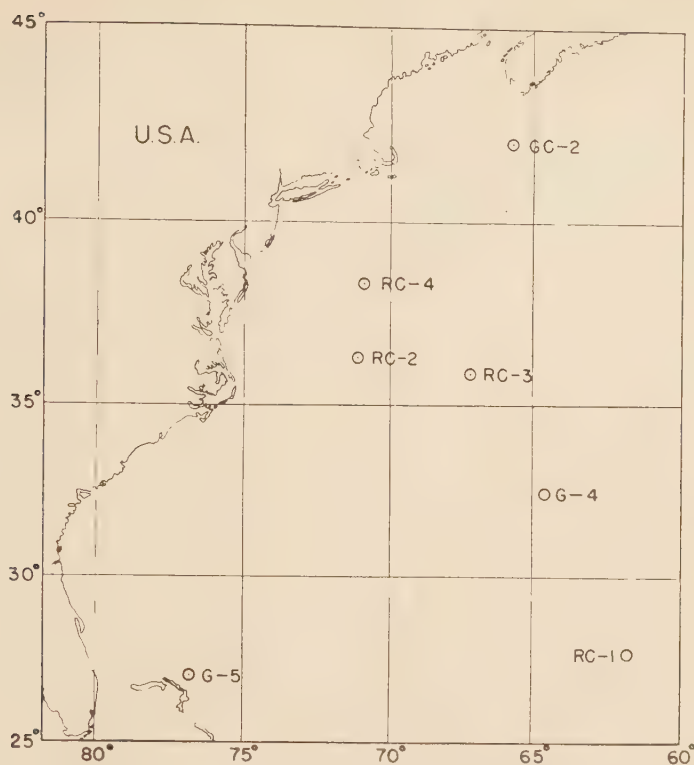


Fig. 1. Geographic location of sediment samples.

Table 1. Geographic location of sediment samples

Sample	Core No.	Location of core	Depth of water
RC-1	A-160 #13 (bottom)	27°45' N, 61°54' W	5667 m
RC-2	A-157 #3 (middle)	36°27' N, 71°12' W	4160 m
RC-3	A-164 #14 (top of lower section)	36°06½' N 67°19' W	4974 m
RC-4	A-164 #2	38°27½' N 70°59' W	3475 m
G-4	A-164 #37 (bottom)	32°34' N, 64°43½' W	1956 m
G-5	A-167 #37 (bottom)	27°08' N, 76°58' W	1829 m
GC-2	A-164 #56 (bottom)	42°09' N, 65°53' W	241 m

The washed coarse material, likewise transferred to a weighing bottle, and heated to constant weight at about 150°C, was found to constitute from 1 to 38 per cent of the total weight of the samples.

The coarse fraction of the sediments used in the present base exchange experiments was examined under the microscope. In the red clays quartz is abundant, and micas and ferro-magnesian are normally present, but little feldspar was found. The coarse fraction of the globigerina oozes showed an almost complete absence of mineral grains.

On the basis of the faunal assemblages* the following conclusions can be drawn:

RC-2: Deposition in a cold climate is indicated by the great abundance of *G. pachyderma*.

RC-3: The poor development of planktonic species suggests that transport of material from shallow water may have taken place.

RC-4: Probably of Miocene or Pliocene age and deposited under reducing conditions. However, there is nothing about the fauna, as it occurs elsewhere in this horizon to indicate deposition during a cold climate.

G-4: The faunal assemblage of this sample is that to be expected in a warm to tropical water environment. Some of the material must have been transported from shallower water, and it is possible that some of the tests have been derived from Pliocene outcrops on the flanks of the Bermuda rise.

G-5: The planktonic assemblage as compared with that of the top of the core indicates a less favourable environment at the time of deposition. There is, however, no definite evidence of lower temperature. It may be that the faunal impoverishment of the past was due to less vigorous oceanic circulation here, rather than lower temperature *per se*.

Inspection under the microscope, x-ray diffraction measurements, and differential thermal analysis were used to determine the mineral constituents of the fine grained portion of the sediments. Quartz, pyroxene, illite group minerals, and some kaolinite group minerals were characteristic of the red clay samples; calcite and illite group minerals of the globigerina ooze samples, and quartz, illite, montmorillonite, and kaolinite group minerals of the green clay sample.

The tracer solutions

In the tracer solutions RaTh and its decay products were present. The concentration of the radioelements was measured in the following manner. An aliquot of solution was evaporated on a glass slide, permitted to stand for an hour, and was then placed just below the phosphor screen of a scintillation counter of a type described elsewhere (KULP *et al.*, 1952). The count rate of the samples was found to vary with time, indicating that RaTh and its disintegration products were not removed from the parent solution in equilibrium amounts. By an analysis of the variation of count rate with time the concentrations of RaTh, ThX, and ThB in the aliquot removed from the parent suspension were calculated.

Base exchange procedure

200 cc mixtures of sediment suspension, radioactive solution, and sea water which had been passed through hardened filter paper were prepared in 250 cc beakers and stirred at constant speed with a Mixmaster type electric stirrer. The suspensions were then centrifuged at ca. 2500 rpm for five minutes, 150 cc of the clear, supernatant liquid placed in a 250 ml beaker, acidified with 2 cc of concentrated nitric acid, and brought up to a volume of 200 cc with distilled water. This procedure removes more than 99% of the clay and all particles larger than 0.1 microns. The sample was then ready for gamma-counting. The remaining liquid was kept for a pH determination, and the sediment was transferred to a sample holder for radioactivity measurements.

Radioactivity analysis of liquid phase

The beakers containing the sample of residual liquid were placed in a finger-type dip Geiger counter. Since the thickness of the Geiger tube window was 30 mg/cm², only beta and gamma radiations were registered. All of the beta and gamma radiations of RaTh and its decay products (except the weak gamma radiation from RaTh) are due to ThB and its decay products. Thus five hours or more after separation of the solid phase, i.e. after equilibrium between ThB and ThC is established, the β - γ radioactivity of the sample reflects the concentration of ThB in the sample. This in turn is determined by the relative initial concentration of ThB, ThX, and RaTh in the solution. An analysis of the curve of count rate versus time, such as is shown in

* The authors are indebted to Mr. D. ERICSON, Submarine Geologist of the Lamont Geological Observatory, for the identification of the animal remains and for the conclusions derived from this information as to conditions of deposition.

Fig. 2, can thus be used to calculate the relative concentration of ThB, ThX, and RaTh in the liquid phase at the time of separation of the sediment by centrifugation.

A determination of the counting efficiency of the dip Geiger counter is necessary for calculating the absolute value of the concentration of these radioelements. This was carried out by determining as a function of time the beta-gamma activity of a sample of stock solution in which the concentration of RaTh had been determined by the scintillation technique described above.

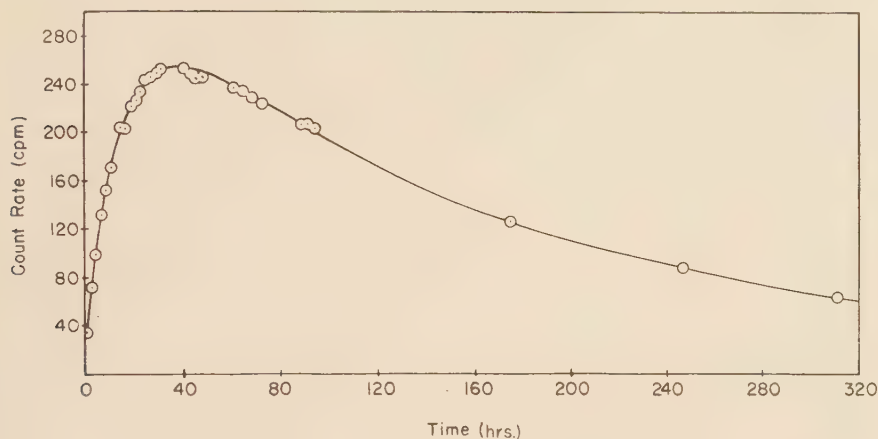


Fig. 2. Count-rate of liquid sample C-84-a.

Radioactivity analysis of the solid phase

The sediment remaining in the centrifuging tubes after the removal of the supernatant liquid was transferred to a sample holder and counted with a 1.4 mg/cm^2 end window Geiger tube. The variation of the count rate as a function of time after preparation of the source was then determined as in the case of the liquid samples. A typical curve is reproduced in Fig. 3. Since

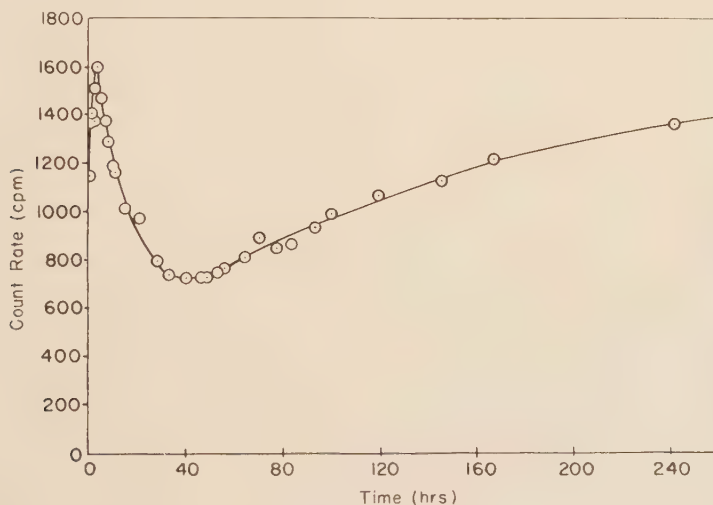


Fig. 3. Count-rate of solid sample C-96-e.

the registered count rate was predominantly due to beta and gamma emission from the sample, the resultant curve of radioactivity versus time reflects the variations in the content of ThB and its decay products in the sample. Qualitatively Fig. 3 indicates that a large excess of ThB has been removed by the sediment from the RaTh solution, that the amount of ThX thus

removed is less than the amount required to support the amount of ThB present in the sediment, and that more RaTh has been removed from the RaTh solution than is in equilibrium with the ThX removed from the solution. Comparison of Fig. 3 with Fig. 2 shows that the qualitative conclusions derived from the two curves agree. This was found to be true in all cases.

II. EXPERIMENTS AND RESULTS

Experiments were designed to test the effect of the nature and concentration of the sediment in suspension, the concentration of the radioelements, and the *pH* on the base exchange of radium and ionium on ocean sediments. Before these variables could be tested, the stirring time required for attaining base exchange equilibrium had to be determined.

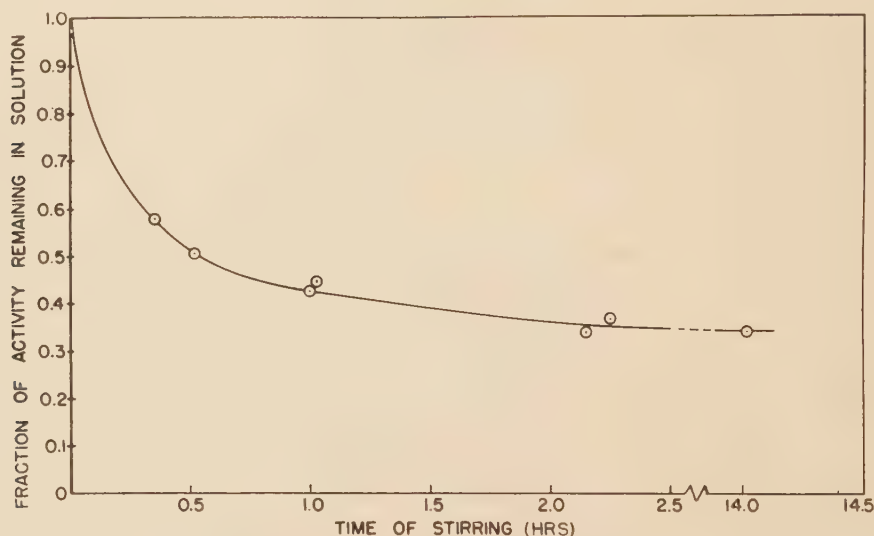


Fig. 4. Relation between stirring time and fraction of activity remaining in a solution containing MsTh_1 and its decay products, after base exchange with red clay.

A weighed amount of dried, powdered, red clay sample RC-1 and an aliquot of solution containing the desired radioelements were added to filtered seawater to give a combined volume of 200 cc. The mixture was then stirred at constant speed for a predetermined time and permitted to settle for an hour. A portion of the clear supernatant liquid was removed, its volume increased to 200 cc with distilled water, and the activity of the solution measured with the liquid finger type Geiger counter. By comparison with the activity of the solution before addition of the sediment, the fraction of activity remaining after base exchange was calculated.

In Fig. 4 the fraction of activity remaining after base exchange which was found in a series of experiments using a solution containing MsTh_1 and its decay products have been plotted as a function of the stirring time. This plot shows that after two hours, continued stirring does not produce a further measurable decrease in the radioactivity of the residual solution. This indicates that base exchange equilibrium was essentially established in approximately two hours for MsTh_2 and ThB, whose concentration was reflected in the measured activity of the residual solution.

A similar rate of approach to adsorption equilibrium has been observed in experiments on the adsorption of calcium on clays by BORLAND and REITEMEYER (1950). Since the mechanism of adsorption is probably similar for most heavy ions,

the rate of approach to adsorption equilibrium might be expected to be similar for ThB, ThX, and RaTh. Nevertheless in the experiments in which equilibrium conditions were desired stirring was continued for 20 to 24 hours to ensure the attainment of base exchange equilibrium.

Table 2. *Data on the effect of total radioelement concentration on the fraction of radioactivity removed by base exchange*

Part 1

<i>Concentration of sediment in the suspension</i>	<i>Volume of radioactive solution used in preparing suspension</i>	<i>Stirring time (hrs)</i>	<i>Fraction of beta-gamma activity remaining in liquid after separation of the sediment</i>
$\mu\text{g RC-1/cc}$	cc MT-1		
101	8.5	0.35	0.57
105	12.4	0.34	0.50 Av. 0.54
105	25.0	0.33	0.50
101	49.5	0.34	0.58
96	0.5	1.00	0.42
106	12.5	1.00	0.33 Av. 0.41
104	50.0	1.03	0.45
99	49.5	1.00	0.43

Part 2

	cc RT-11		
104	5.0	0.33	0.44
96	10.0	0.33	0.44 Av. 0.43
100	15.0	0.35	0.42
103	5.0	1.00	0.35
96	10.0	1.00	0.31 Av. 0.33
101	15.0	1.00	0.33

In the course of determining the stirring time necessary to attain base exchange equilibrium the effect of the concentration of the radioelements in the sediment-sea water suspension on the quantity of the radioelements absorbed was studied. The results are shown in Table 2. From this it follows that the fraction of radioactivity remaining after separation of the sediment is independent of the total quantity of the radioelements in the system. This is in agreement with the law of mass action as might be expected at the extremely low concentrations used in these experiments.

Experiments as described above were carried out at equilibrium with samples of red clay, globigerina ooze, and green clay. The initial and final concentration of the radioelements, and the ratio of the weight of radioelement in the solid and liquid phase at the end of the experiment are listed in Table 3. In Figs. 5 and 6 the ratio of the quantity of RaTh and ThX in the solid phase to the quantity in

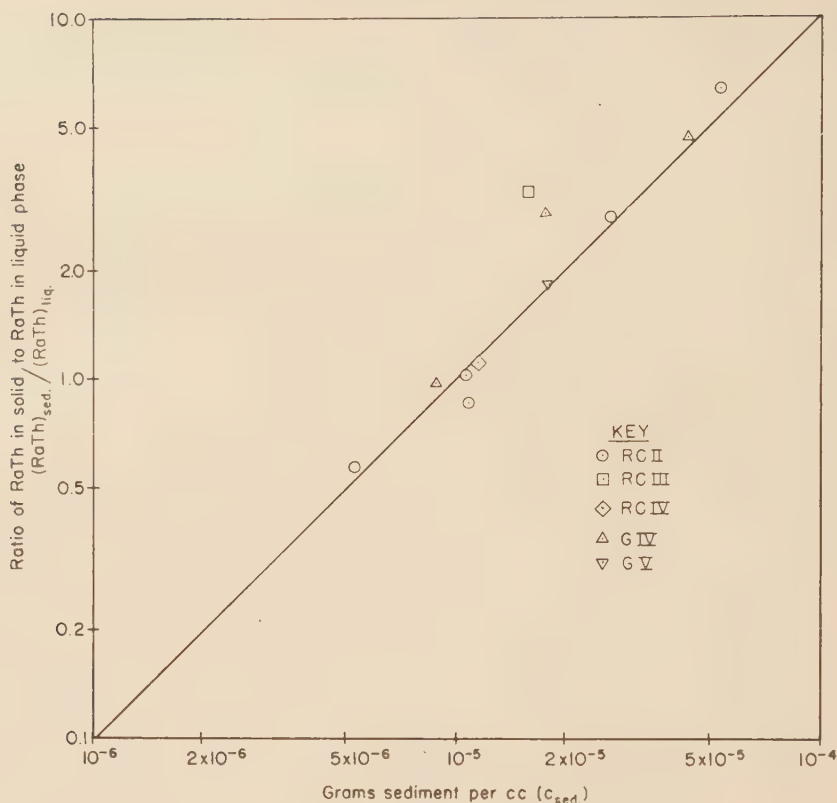


Fig. 5. Ratio of RaTh in the solid phase to that in the liquid phase at equilibrium as a function of the concentration of the sediment in the suspension.

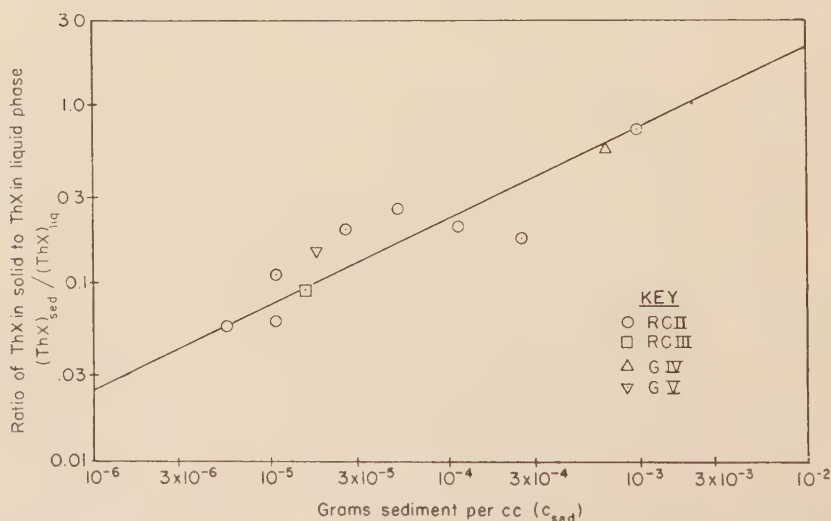


Fig. 6. Ratio of ThX in the solid phase to that in the liquid phase at equilibrium as a function of the concentration of the sediment in the suspension.

the liquid phase at equilibrium have been plotted as a function of the concentration of sediment in the suspension. It can be seen that a line of unit slope best fits the data on the distribution of RaTh between the sediment and the liquid phase. Thus

$$\frac{(\text{RaTh})_{\text{sed}}}{(\text{RaTh})_{\text{liq}}} = c_{\text{sed}} \times 10^5 \quad (1)$$

where c_{sed} is the concentration of sediment in the suspension in gm/cc; the quantity of RaTh adsorbed per gram of sediment is therefore directly proportional to the concentration of RaTh in the liquid phase.

The data for the samples of red clay and globigerina ooze fall on approximately the same straight line. The data for the sample of green clay are erratic but fall below the points for red clay and globigerina ooze. As can be seen from an inspection of Table 3 a reduction of the pH decreases the adsorption of RaTh on the sediment.

The data for the adsorption of ThX on the sediment samples, shown in Fig. 6, cannot be fitted by a line of unit slope. The line of best fit obeys the relationship

$$\frac{(\text{ThX})_{\text{sed}}}{(\text{ThX})_{\text{liq}}} = 19 (c_{\text{sed}})^{0.48} \quad (2)$$

from which it follows that in these experiments the weight of ThX adsorbed per gram of sediment was a function of the sediment concentration as well as of the concentration of ThX in the liquid phase. Again it was found that the data for the red clay and globigerina ooze samples fell along the same line. Very little ThX was removed from the liquid phase by adsorption on the green clay sample.

Discussion of errors

In carrier-free tracer experiments there are many sources of error which become trivial in systems in which macroscopic quantities of reagents are used. Some of the most probable sources of error in the measurement of the distribution of the radioelements between the solution and adsorbent are as follows:

1. Extraneous wall effects. Since wall effects were found to be important in the storage and removal of radioactive solutions, it is possible that occasional particles of dirt or grease on the walls of the glassware used during the base exchange procedure were the cause of errors.

2. Errors in transferring sediment from the parent suspension. Settling of the suspension in the pipette during withdrawal occurred within the parent suspension. This was particularly noticeable when the volume removed by means of the pipette was relatively large.

3. Incomplete removal of sediment from the residual solution. Decanting of the supernatant liquid after centrifuging may have caused the transfer of a small amount of sediment to the residual solution.

4. Errors in measuring the radioactivity of samples. Errors due to the variations in the counting geometry probably affected the liquid sample results only slightly. This was indicated by repeated checks on the count rate at short time intervals, and the normally smooth variation of the count rate with time.

Evaporation took place slowly during the 200 hour period during which the activity of the residual solution was measured. However, it was found that the count rate of samples whose volume had decreased from 200 to 180 cc during the period of observation was not changed appreciably by restoring the volume to 200 cc by addition of distilled water.

Table 3. Base exchange data for experiments at equilibrium

Sedi- ment Sample	Run No.	Concentra- tion of sediment in suspension ($\mu\text{g/cc}$)	pH	Weight of RaTh absorbed on sediment in 10^{-13} gm/cc (RaTh) _{sed}	Weight of RaTh in liquid phase in 10^{-13} gm/cc (RaTh) _{liq}	$\frac{(\text{RaTh})_{\text{sed}}}{(\text{RaTh})_{\text{liq}}}$	Weight of ThX absorbed on sediment in 10^{-15} gm/cc (ThX) _{sed}	Weight of ThX in liquid phase in 10^{-15} gm/cc (ThX) _{liq}	$\frac{(\text{ThX})_{\text{sed}}}{(\text{ThX})_{\text{liq}}}$
RC-2	1	5.3	6.6	0.39 $\pm$ 0.11	0.69 $\pm$ 0.06	0.57	0.10 $\pm$ 0.10	1.89 $\pm$ 0.05	0.05
	2	5.3	6.8						
	3	10.7	6.7	0.64 $\pm$ 0.13	0.62 $\pm$ 0.70	1.03	0.16 $\pm$ 0.13	1.88 $\pm$ 0.06	0.11
	4	10.7	6.8	0.50 $\pm$ 0.11	0.58 $\pm$ 0.06	0.86	0.11 $\pm$ 0.23	1.38 $\pm$ 0.12	0.06
	5	26.7	6.8	0.94 $\pm$ 0.10	0.32 $\pm$ 0.04	2.94	0.26 $\pm$ 0.12	1.28 $\pm$ 0.05	0.20
	6	27.7	6.8						
	7	26.7	3.4	0.13 $\pm$ 0.05	0.30 $\pm$ 0.02	0.43	0.02 $\pm$ 0.14	0.75 $\pm$ 0.07	—
	8	53.5	6.8	0.09 $\pm$ 0.08	0.17 $\pm$ 0.02	6.4	0.32 $\pm$ 0.13	1.22 $\pm$ 0.06	0.26
	9	53.5	6.8						
	10	107	7.1	1.26 $\pm$ 0.06	nil	—	0.24 $\pm$ 0.14	1.17 $\pm$ 0.08	0.21
	11	267	6.8	1.40	nil	—	0.24 $\pm$ 0.15	1.30 $\pm$ 0.08	0.18
	12	267	6.8	1.40	nil	—			
	13	267	6.8	0.25	nil	—	0.02 $\pm$ 0.06	0.34 $\pm$ 0.03	0.06
	14	1070	6.8	1.26	nil	—	0.60 $\pm$ 0.16	0.81 $\pm$ 0.16	0.74
	15	1070	6.8	1.26	nil	—			
RC-3	16	15.9	8.1	0.60 $\pm$ 0.06	0.19 $\pm$ 0.02	3.2	0.08 $\pm$ 0.05	0.92 $\pm$ 0.05	0.09
17	15.9	8.1							
RC-4	18	11.7	8.2	0.51 $\pm$ 0.07	0.46 $\pm$ 0.02	1.1	0.00 $\pm$ 0.10	1.33 $\pm$ 0.06	0.00
19	11.7	8.2				0.00 $\pm$ 0.010	1.58 $\pm$ 0.07	0.00	
G-4	20	8.9	8.2	0.21 $\pm$ 0.05	0.22 $\pm$ 0.02	0.96	0.03 $\pm$ 0.10	0.72 $\pm$ 0.05	—
	21	17.8	7.5	0.94 $\pm$ 0.11	0.32 $\pm$ 0.05	2.9	nil $\pm$ 0.14	1.51 $\pm$ 0.07	—
	22	44	7.7	1.04 $\pm$ 0.08	0.22 $\pm$ 0.02	4.7	0.06 $\pm$ 0.14	1.48 $\pm$ 0.14	—
	23	89	8.1	1.26 $\pm$ 0.06	nil	—	nil $\pm$ 0.14	1.54 $\pm$ 0.07	—
	24	780	8.2	1.26 $\pm$ 0.06	nil	—	0.56 $\pm$ 0.12	0.98 $\pm$ 0.05	0.57
G-5	25	18.2	8.2	0.44 $\pm$ 0.07	0.24 $\pm$ 0.04	1.8	0.30 $\pm$ 0.17	2.00 $\pm$ 0.06	0.15
26	18.2	8.2							
GC-2	27	6.7	8.2	0.07 $\pm$ 0.09	0.36 $\pm$ 0.04	0.19	0.02 $\pm$ 0.10	0.73 $\pm$ 0.10	—
	28	13.3	8.3	0.16 $\pm$ 0.10	0.27 $\pm$ 0.05	0.59	nil $\pm$ 0.14	1.54 $\pm$ 0.07	—
	29	13.3	7.0	1.01 $\pm$ 0.09	0.25 $\pm$ 0.03	4.0	0.13 $\pm$ 0.07	0.61 $\pm$ 0.03	0.21
	30	13.3	3.4	0.08 $\pm$ 0.06	0.35 $\pm$ 0.03	0.23	0.15 $\pm$ 0.07	0.60 $\pm$ 0.03	0.25
	31	33.2	8.2	0.26 $\pm$ 0.05	0.17 $\pm$ 0.05	1.53	0.11 $\pm$ 0.07	0.63 $\pm$ 0.07	0.17
	32	33.2	8.2	0.73 $\pm$ 0.10	0.24 $\pm$ 0.05	3.0	—	—	—
	33	33.2	3.3	0.14 $\pm$ 0.06	0.29 $\pm$ 0.03	0.48	0.09 $\pm$ 0.07	0.68 $\pm$ 0.03	0.14
	34	33.2	3.5	0.10 $\pm$ 0.06	0.33 $\pm$ 0.03	0.30	0.11 $\pm$ 0.07	0.63 $\pm$ 0.03	0.18
	35	66.5	8.4	0.78 $\pm$ 0.04	nil	—	0.05 $\pm$ 0.05	0.95 $\pm$ 0.05	—
	36	66.5	3.8	0.79 $\pm$ 0.04	nil	—			
	37	1330	7.0	1.26 $\pm$ 0.06	nil	—	0.04 $\pm$ 0.14	1.50 $\pm$ 0.07	—

The statistical counting error was generally kept below 1 per cent by observing the count rate over sufficiently long periods of time.

5. Errors in graphical analysis. The method of calculation causes a compounding of errors so that the most reliable data should be those for RaTh, the least reliable those for ThB. Large percentage errors were unavoidable when either little removal or almost complete removal of a radioelement by chemisorption on the sediment had taken place.

IV. GEOLOGIC SIGNIFICANCE OF BASE EXCHANGE EXPERIMENTS

In the oceans the concentration of radium and of ionium must be reasonably constant. The time required for a particle of sediment to fall from the surface to the ocean floor must be long enough for the ions to equilibrate between the solid and liquid phases. Therefore, if the important mechanism of removal of radium and ionium is indeed base exchange, the concentrations of these elements on the surface of ocean sediments predicted on the basis of an extrapolation of the experimental adsorption data to the actual concentration of these elements in sea water, will agree with the concentrations of these elements actually found in ocean sediments.

The data for the adsorption of RaTh on red clay and globigerina ooze are readily extrapolated to the concentrations encountered in sea water since it was found that the law of mass action is directly obeyed. The concentration of ionium in sea water is $(3.1 \pm 1.0) \times 10^{-15}$ gm/cc (HOLLAND and KULP, 1954), so that the predicted concentration of ionium on the sediments studied is

$$\frac{(\text{Io})_{\text{sed}}}{c_{\text{sed}}} = (\text{Io})_{\text{liq}} \times 10^5 = 3.1 \times 10^{-15} \times 10^5 = 3.1 \times 10^{-10} \text{ gm/gm}$$

As can be seen from Table 4 this value agrees well with that to be expected for the sediments studied.

Extrapolation of the base exchange data for ThX is not as readily justified since the sediment concentration in the oceans is involved in the calculation. Assuming the figure proposed by KULLENBERG (1953) for the average concentration of sediment in the open ocean, and a value of 3×10^{-17} gm/cc for the average concentration of radium in ocean water (RONA and URRY, 1952), we derive from equation (2)

$$\begin{aligned} \frac{(\text{Ra})_{\text{sed}}}{c_{\text{sed}}} &= 19 (c_{\text{sed}})^{-0.52} (\text{Ra})_{\text{liq}} = 19 \times (5.6 \times 10^{-8})^{-0.52} \times (3 \times 10^{-17}) \\ &= 3 \times 10^{-12} \text{ gm/gm.} \end{aligned}$$

As in the case of ionium this figure agrees well with the experimentally determined value of the quantity of radium adsorbed on sediments of the type studied in these experiments. These data therefore show that base exchange processes are largely responsible for removal of ionium and radium from ocean water with ocean sediments. It is significant that the adsorption data not only predict the observed range of concentration of excess radium and ionium but also suggest that the disequilibrium between ionium and uranium is greater than that between radium and uranium in recently deposited ocean sediments. This shows that the interpretation of the radium versus depth curves in cores of ocean sediment given by PIGGOT and URRY (1941) is correct, and therefore gives theoretical support for the ionium method of age determination.

It has been observed by URRY (1949) and VOLCHOK and KULP (1954) that the curve of radium versus depth in heterogeneous deep sea cores cannot be explained in terms of a single ionium decay curve. In view of the above conclusions this is not surprising, for, since the concentration of excess radium and ionium in deep sea sediments appears to be controlled by base exchange phenomena, only sediment layers which have similar base exchange properties might be expected to yield points lying on a single ionium decay curve. However, that this is not a very severe restriction to the applicability of the method of age determination is suggested by the close agreement shown in Figs. 5 and 6 between the base exchange properties of several types of sediments. The most critical factor appears to be the absolute surface area of the sediment, and experiments are under way at the Lamont Observatory to examine quantitatively the relationships between this property and the radium and ionium content of heterogeneous cores of ocean sediment.

Table 4. *Predicted and observed adsorption of ionium and radium in deep sea sediments*

<i>Ion</i>	<i>Con. in sea water g/cc</i>	<i>Reference</i>	<i>g adsorbed/g sediment from base exchange data</i>	<i>g adsorbed/g sediment experimental range</i>	<i>Sed. similar to RC-2 and G-4</i>
Ionium	$3.1 \pm 1.0 \times 10^{-15}$	(HOLLAND and KULP, 1954)	$3 \pm 2 \times 10^{-10}$	1 to 20×10^{-10} *	2 to 5×10^{-10}
Radium	$3.1 \pm 0.5 \times 10^{-17}$	(RONA and URRY, 1952)	$3 \pm 2 \times 10^{-12}$	0.1 to 40×10^{-12} †	1 to 10×10^{-12}

* ISAAC and PICCIOTTO, (1953).

† PIGGOT and URRY, (1941), URRY and PIGGOT, (1942), URRY, (1949).

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The geological significance of variations in the abundances of the isotopes of silicon in rocks

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(Received 5 February 1954)

ABSTRACT

Physical and chemical processes which may lead to variations in the isotopic content of rocks are discussed in this paper, with special emphasis given to the processes of chemical exchange which may occur during the early stages of formation. Quantitative calculations deriving from physical understanding of these mechanisms have been applied whenever possible to the case of silicon, and lead to certain conclusions relating the isotopic abundances of silicon to the geological history of the mineral. They are: (i) limits may be calculated for the isotopic content of rocks which formed in equilibrium from a common magma, (ii) it is unlikely that diffusion processes play any part in the separation of silicon isotopes, either in the solid or liquid state, (iii) analysis of abundances in a given mineral can reveal whether or not sedimentation during its history is a necessary hypothesis. The paper is entirely theoretical, and except for a few minor extensions to existing methods, it contains no original developments.

INTRODUCTION

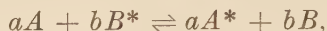
Isotopes and the problems of their natural distribution and abundance are not a new field of interest for geophysicists and geochemists. The "uranium clock" method of determining the ages of minerals through the abundances of the radioactive isotopes of their lead has been a specific concern of geophysicists for some time; and during more recent years problems associated with the distribution of isotopes of the lighter elements in organic and inorganic materials have entered the field of study of the geochemist, biologist and archaeologist. A relatively new facet of this well-established field, however, is—to geological science at least—the investigation of isotopic exchange reactions and their geological significance. Since the equilibrium exchange of isotopes between molecules was first conceived and investigated (cf. UREY, 1935) it has been recognized as a quantum effect. Since then, highly precise measurements of the isotopic abundances of the lighter elements have been made with mass spectrometers among a wide variety of substances and the results have been compared with the predictions of quantum statistical mechanics. The agreement has been excellent (UREY, 1947). Such a background invites a considerable amount of confidence in the use of isotopic abundances as a probe for exploring geological histories and for unravelling the mysteries of geological origins. The isotopes of oxygen (SILVERMAN, 1951; UREY and others, 1951) and of sulphur (THODE, McNAMARA and COLLINS, 1949) have already been the subject of such studies; it seems natural that those of silicon, the second-ranking element in natural abundance on the surface of our planet, should receive similar attention.

This paper is intended merely to be an ancillary aid in the interpretation of the geological significance of the measurements of silicon isotopic abundances made by ALLENBY (1953) which are given in a separate paper. It does not claim any original contribution to scientific knowledge; the methods which are used here have been used several times before, in the same way and upon similar

problems. The difference is one only of detail in the application of these principles to a particular new case.

ISOTOPIC ABUNDANCES AND EQUILIBRIUM EXCHANGE REACTIONS

In a system composed of two substances in thermodynamic equilibrium, whose molecules A and B have an element in common, the isotopic exchange reaction is



in which the superscript indicates the molecule containing the heavier isotope of the common atom. The equilibrium constant K of this reaction may be expressed in terms of the changes in the zero-point energy of the two molecules, as the isotopes are interchanged:

$$-RT \ln K = a\Delta E_A^0 - b\Delta E_B^0 - aRT \ln \left(\frac{Q^*}{Q} \right)_A + bRT \ln \left(\frac{Q^*}{Q} \right)_B$$

where the Q 's are the partition functions of the molecules. This expression is equivalent to

$$K = \left(\frac{Q_A^*}{Q_A} \right)^a \cdot \left(\frac{Q_B^*}{Q_B} \right)^{-b} \cdot e^{-\frac{a\Delta E_A^0 - b\Delta E_B^0}{RT}} \quad (1)$$

and so it appears that calculations of K involve only the ratios of the partition functions of the ordinary and the isotopic molecules, which is a piece of good fortune, since these ratios may be calculated with far greater accuracy and simplicity than the partition functions themselves. The method that is usually adopted makes the assumption that the kinetic energy of each molecule can be separated completely into its various components, viz., translational, rotational, vibrational, etc., and that there is no coupling between one type of motion and another. Strictly speaking, this assumption is true only for ideal gases at moderate temperatures, but it serves as an approximation to the behaviour of ordinary molecules under many circumstances. It has been shown how, when this condition is fulfilled and when the temperature at which the reaction takes place is sufficiently high that all the vibrational levels are fully excited, the partition functions can be expressed in terms of the fundamental eigenfrequencies ν_i of the internal vibrations of the molecule (UREY, 1947). The expression that results for K is

$$K = \left[\frac{\sigma_A}{\sigma_A^*} (1 + \sum_i G(u_i) \Delta u_i)_A \right]^a / \left[\frac{\sigma_B}{\sigma_B^*} (1 + \sum_i G(u_i) \Delta u_i)_B \right]^b \quad (2)$$

where $u_i = \frac{h\nu_i}{kT}$, and $\Delta u_i = u_i - u_i^*$ (which is always positive), and where the function $G(u) = \frac{1}{2} - \frac{1}{u} + \frac{1}{e^u - 1}$ has been tabulated by BIGEISEN and MAYER (1947). The symmetry numbers σ are introduced into the calculations because of the fact that isotopic substitution sometimes lowers the symmetry of the molecule, causing a splitting of the degenerate rotational energy levels, and thereby altering

the contribution to the partition function from the rotational motion. If the ν_i are known (usually from infrared or Raman spectra) then the isotopic shifts may be found by applying the Teller-Redlich rule and the equilibrium constant, K , may then be calculated theoretically from these data alone. It may be remarked that the only physical variable in the expression (2) is the temperature T ; therefore the equilibrium constant appears to be an explicit, monotonically decreasing function of temperature.

The "enrichment factor," or the ratio by which one of the substances is expected to be enriched in the heavy isotope at the expense of the other, is equal to K when only one nucleus in each molecule is exchanged, i.e. when $a = b = 1$. When more than one atom of the isotopic element is contained in one or both of the molecules, however, it is generally assumed that the heavy isotope is distributed randomly through the assemblage, and that (*a priori*) the probability of exchange of this isotope amongst the molecules of species A , let us say, is governed by the symmetry numbers alone of the various isotopic configurations for A . This assumption appears to be a good approximation for all substances in which the isotopic nuclei occupy equivalent positions in the molecule, except if the isotopes be those of hydrogen (UREY and GREIFF, 1935) and in view of the intractable complexity of the calculations of the frequencies of the mixed type of molecule, this assumption must be made in any case. If the number of the isotopic nuclei in the molecule is S , then the enrichment factor becomes equal to $K^{1/S}$.

THE STRUCTURE OF SILICATES

The crystalline structures of most of the more common silicate minerals have been known for some time from x-ray diffraction and optical measurements (BRAGG, 1930, 1937). They are constructed of a common building block, consisting of four atoms of oxygen and one of silicon. The oxygen nuclei lie at the corners of a regular tetrahedron and the silicon nucleus lies at the centre, the whole constituting an arrangement of unusual stability. Under certain conditions, these tetrahedral ions "polymerize" by sharing one or more corners, the shared atom frequently being spoken of as an "oxygen bridge." By linking themselves one to another in this way, the ions are capable of forming numerous configurations such as endless chains, closed rings, helixes, polyhedra, infinite sheets, and the like. The net charges of these polymers are balanced by the metallic cations such as sodium, potassium, and aluminium.

In order to apply the methods of statistical mechanics to the calculation of enrichment factors for the isotopes of silicon in silicates, it must be assumed that the probability of the exchange of silicon atoms between molecules of different species is governed exclusively by the internal motions of the SiO_4 ion, and that the group symmetry characteristics of the vibrational modes are not destroyed by polymerization. Such an assumption is necessary from a purely practical standpoint in view of the enormous complexity of the molecules of most silicate minerals, and because the hopeless intractability of the normal equations precludes the complete interpretation of their infrared spectra by the ordinary procedures of group theory. It should be reasonably valid for orthosilicates such as topaz, zircon, olivine, etc., which have no oxygen bridges; but on the other hand it very

probably becomes progressively worse among the more highly developed polymer networks, for admittedly it is difficult to see how some of the fundamental modes of the tetrahedral group can survive at all among the more complicated crystal structure types, much less without serious changes in their symmetry.

The infrared reflection spectra of a wide selection of silicate crystals (SCHAEFER, MATOSSI and WIRZ, 1934; MATOSSI and KRÜGER, 1936) demonstrate the dominant part that is played by the internal vibrations of the SiO_4 ion in the infrared activity of silicates. They also suggest that in general the frequencies increase with increasing polymerization or, in different words, with an increasing proportion of "oxygen bridges," but that the effect is not very large. It was noted, however, that the bands tend to become more broad and diffuse among the more highly developed polymers, suggesting distortion of the fundamental modes, and making their frequencies less distinctly identifiable.

No account is taken, in the simple picture framed by our working hypothesis, of the contribution to the equilibrium constant from the motion of the silicon nuclei due to the lattice vibrations of the crystal, or the "acoustic spectrum," which is also quantized. One might expect, however, that such effects, if they exist at all, would be smaller by many orders of magnitude than those which we have been discussing.

In the theory of crystallization, the essential distinction between a melt and a crystal is said to consist in the order and motion of the ions. At the temperature of crystallization a highly ordered arrangement becomes thermodynamically stable, or in other words, the ionic activity becomes less in the ordered state than in the melt. Now the entropy of fusion of silicates is not high, and so no major changes in structure should be expected to take place upon melting. Thus the liquid structure in many respects closely resembles the solid, with the result that partition functions and other molecular constants should be very little affected by the change of state (cf. ZACHARIASEN, 1932). The liquid melts have in fact been shown to possess an ionic constitution, in which the metallic cations are free to move and the anions are polymerized SiO_4 tetrahedra linked by oxygen bridges in various networks which are similar to those found in solid crystalline silicates (BARTH and ROSENQVIST, 1949). The more strongly polarizing cations, however, such as the alkali metals, tend to discourage polymerization in the melt and to favour the formation of individual SiO_4 groups, at the same time increasing the activity of the highly polymerized silicon-oxygen anions (EITEL, 1941). Under certain conditions, therefore, melts high in SiO_4 concentration will separate from melts of highly polymerized networks; such a phenomenon is termed separation into ortho-silicate and para-silicate melts, respectively, and is closely related to the differentiation of a magma into the ferromagnesian (orthosilicate) and the feldspar (parasilicate) reaction series of BOWEN. Consequently the partition functions of orthosilicate melts, wherever strongly polarizing cations are present, should very closely approximate that of the SiO_4 ion.

THE FUNDAMENTAL FREQUENCIES OF SiO_4

Group theory tells us that a tetrahedral group of atoms has nine different normal modes of vibration, but because of the high degree of symmetry, several of these

modes are degenerate, and the total number of different frequencies is reduced to four. Their classification is as follows:

<i>Mode,</i>	<i>Degeneracy</i>	<i>Active or Inactive</i>	<i>Nuclei in Motion</i>	<i>Type of displacement</i>
ν_1	Non-degenerate	Inactive	O's	Pulsation along Si-O bond length
ν_2	two-fold degenerate	Inactive	O's	$\perp$ to Si-O bond lengths
ν_3	three-fold degenerate	active	Si, O's	translational
ν_4	three-fold degenerate	active	O's	Deformational oscillation along and $\perp$ to Si-O bond lengths

Of these, only the ν_3 mode is affected by isotopic substitution of the silicon nucleus, therefore it is the only mode that contributes to the exchange probability for silicon. Once ν_3 is known, $\Delta\nu_3$ may be calculated by the Teller-Redlich product rule (HERZBERG, 1945), according to which

$$\frac{\nu_3^*}{\nu_3} = \left[\frac{\text{Si}^{28}}{\text{Si}^{30}} \cdot \frac{\text{Si}^{30} \cdot \text{O}_4}{\text{Si}^{28} \cdot \text{O}_4} \right]^{\frac{1}{2}} = 0.97654$$

so that $\Delta\nu_3 = 0.02346\nu_3$.†

The only silicates whose Raman spectra have been recorded up to the present time, to the writer's knowledge, are topaz (KRISHNAN, 1947; NISI, 1932), phenacite (NARAYANAN, 1950; NISI, 1932), and zircon, danburite and beryl (NISI, 1932), but no attempt has been made at their interpretation. The positions of the SiO_4 frequencies in the spectrum, however, are known qualitatively from the works of SCHAEFER, MATOSSI, WIRZ, and KRÜGER on infrared reflection. They found that certain dominant reflection bands occurred in all of the spectra with maxima at about 500 cm^{-1} , $500\text{--}600 \text{ cm}^{-1}$, 800 cm^{-1} , and $900\text{--}1100 \text{ cm}^{-1}$, and these they identified with the ν_2 , ν_4 , ν_1 and ν_3 modes, respectively, of the SiO_4 group.¶

For silicates other than these five, theoretical calculations of enrichment factors must wait until more Raman data are available. MATOSSI (1949) has developed from group theory an ingenious system for calculating the fundamental modes of a wide variety of SiO networks and structure types, but the formulae generally contain molecular force constants which in the main can be determined only by direct spectroscopic measurement. MATOSSI made several calculations

† In actual practice, one might expect the degenerate modes to be split up owing to deformation of the tetrahedral bonds by lattice binding, and experiment confirms this (LECOMTE, 1948); consequently ν_3 and ν_4 may be expected to appear as triplet lines, and ν_2 as a doublet, in actual Raman spectra.

¶ The correctness of the assignment of ν_1 , the "breathing oscillation" or the pulsation mode, to a wave number of about 800 cm^{-1} has since been corroborated independently by the work of MICHALKE (1938) on the polarization of Raman lines in crystals, and that of MATOSSI and BRONDER (1938) on infrared absorption spectra.

by determining the Si-O force constants in topaz or one of the other orthosilicates, and assuming the same values for the polymerized parasilicates; and although these calculations claim only a qualitative correctness they are nevertheless interesting, since they predict what was observed beforehand, viz., that the frequencies increase with the number of oxygen bridges.

Unlike other silicates, low temperature quartz cannot be subdivided into SiO_4 groups. The structure of α -quartz is described by BRAGG and BRAGG (1935): the smallest repeating unit consists of three bent SiO_2 triplets spaced at equal intervals in the vertical direction, each turned through 120° with respect to its predecessor and tilted out of the horizontal plane, so that the nuclei follow a sort of spiral about an axis of three-fold rotational symmetry. The packing is described as trigonal trapezohedral; it is such that the Si and O atoms are arranged in parallel planes, with each Si atom apparently surrounded by four O atoms, and each O atom with two Si neighbours.

An interpretation of the Raman spectrum of α -quartz has been worked out by SAKSENA (1941) on the basis of the methods of group theory developed by WIGNER. According to his scheme, each of the observed Raman frequencies is assigned to a particular symmetry mode, which is not actually a description of a normal mode of vibration of the lattice, but rather a description of the form of displacement that may be associated with the symmetry coordinates of the unit cell. When considering the lattice as a whole, all of the equivalent points of the lattice must have the same motion at each instant. In a continuously linked structure like quartz, this naturally would lead one to suspect that neighbouring cells influence one another's motion; but if the amplitudes of the vibrations are small, the extent of this influence will be very slight. The normal vibrations of a given class will be particular linear combinations of the symmetry modes falling within that class; but their actual determination would require a full and detailed knowledge of the force constants within the crystal lattice, which is not available. However, a different symmetry mode will predominate in each normal mode, and so by a less rigorous procedure one may associate each of the lines with its dominant symmetry mode and calculate the isotopic shifts accordingly, understanding that these values may be expected to be only qualitatively correct.

The allocation of the Raman frequencies among the symmetry modes of the quartz cell has been made partly by theoretical reasoning and partly on the basis of experimental evidence gained from a detailed laboratory study of the Raman spectrum of α -quartz, using incident light polarized in different azimuths as well as unpolarized light, and for different orientations of the crystal. By correlating the results with existing data on infrared reflection and absorption spectra, and making use of certain deductions from the theory of light scattering and of infrared absorption, SAKSENA was able to assign every line uniquely; and on the basis of this interpretation he calculated the specific heat of α -quartz over a wide range of temperatures by the Einstein-Debye theory, and found his calculations to be in good agreement with experimental values.

At about 575°C , the quartz cell rearranges itself from a trigonal trapezohedral to a hexagonal symmetry, the transformation commonly being spoken of as the transition from low-temperature to high-temperature quartz. There is an inherent

tendency for large crystals of high-temperature quartz to fracture spontaneously; and as a result, its Raman spectrum has been observed only partially (NARAYANASWAMY, 1948). Attempts to calculate the fundamental frequencies from group theory using the force constants determined for α -quartz (SAKSENA and NARAIN, 1949) have met with only moderate success, and so it appears that the data for β -quartz are not yet at a stage that is useful for the calculation of isotopic exchanges.

EXAMPLES

1. Quartz-Topaz

As a first example of the application of these methods, let us consider a system of low-temperature quartz and topaz in thermodynamical equilibrium. The reason for this choice is that both are low-temperature hydrothermal minerals, and therefore the isotopic separation should be relatively large.

The structure of topaz has been determined by PAULING (1928). The repeating unit is an orthorhombic parallelepiped consisting of four molecules $(\text{Al, F, OH})_2\text{SiO}_4$, or 52 atoms in all. Because of the low symmetry, nearly all possible modes of vibration should be active both in the Raman effect and in infrared absorption. The Raman spectrum of topaz has been recorded in excellent detail by KRISHNAN (1947) and in it there appear three intense lines at 920, 934 and 985 cm^{-1} which probably correspond to the three members of the ν_3 mode of the SiO_4 group. The comparatively wide separation of the highest frequency from the other two is possibly due to anisotropy of scattering within the crystal, since it has a positive optic axis. Another strong triplet appears at 241, 269 and 287 cm^{-1} , a doublet at 520 and 558 cm^{-1} , and a very intense single line at 770 cm^{-1} , and if these groups are identified with the ν_4 , ν_2 and ν_1 modes, respectively, of the SiO_4 ion, the whole interpretation accords very well with the formula of DENNISON (1925) and SCHAEFER (1930) for the normal frequencies of a tetrahedral molecule.

For quartz, SAKSENA's interpretation is used, and the isotopic shifts are calculated from the symmetry modes of the unit cell, by applying the rule of TELLER and REDLICH. The enrichment factor for Si^{30} in quartz is then found to be

$T^\circ\text{C}$	E (quartz: topaz)
108	1.011
203	1.008
292	1.006
377	1.005

Thus it appears that under the ideal conditions that are assumed to prevail by the postulates of statistical mechanics, quartz should contain not more than 0.6% more Si^{30} than topaz if the two were formed in equilibrium at 300°C, and less if the temperature of formation were higher. Perhaps this may seem rather an academic exercise in view of the fact that most vein silica, including quartz and topaz, is deposited by circulating waters, so that unless a high reaction velocity exists for the exchange, it is probable that equilibrium is never attained at all; and further, in waters with high concentrations of silica, the mineral is largely transported not in the ionic state as we have assumed in our theory, but in the

colloidal state (ROY, 1945) about which we know very little. Nevertheless this figure is an interesting one to keep in mind, for inasmuch as every failure to fulfil the assumptions of the statistical theory tends to diminish the answer, the figure that obtains when these premises are fully satisfied represents the maximum effect that may be expected from the equilibrium process.

2. *Orthosilicate-Parasilicate melts*

If all igneous rocks are derived from a common magmatic origin—as some geological theories enjoin—which separates spontaneously into an orthosilicate (unpolymerized) and a parasilicate (polymerized) phase, then it becomes of practical interest to determine how isotopes ought to be divided up by this separation. To do so we must assume that the processes of differentiation are sufficiently slow in comparison with the reaction rate for isotopic exchange, that the equilibrium for this exchange is attained at every step in the sequence and is never very seriously disturbed for any length of time. This hypothesis can scarcely be questioned, because the process of magmatic separation is intrinsically an equilibrium process; and in view of the enormous viscosities that exist in silicate melts, the separation must proceed so slowly that complete thermodynamic equilibrium should prevail at all times. This being so, and recalling the structural similarity that exists between silicate crystals and silicate melts, statistical mechanics should give a good idea of the expected distribution. It is known that the internal frequencies of the SiO_4 ion increase with the silica content of the rock, the ν_3 mode ranging from about 900 cm^{-1} for the most silica-poor to about 1100 cm^{-1} for the most silica-rich. Now the symmetry number of the SiO_4 group is unaffected by an isotopic substitution for the silicon nucleus; consequently since $G(u)$ is a monotonically increasing function of u , formula (2) tells us that the high-silica phases should be enriched in the heavy isotope, and the low-silica phases should be correspondingly impoverished. To be more specific, let us take 900 cm^{-1} and 1100 cm^{-1} as the lower and upper limits of the wave number of the ν_3 mode in silicates; then it turns out that the enrichment factor for Si^{30} between the extreme limits of silica-rich and silica-poor rocks, which have formed in equilibrium, should not exceed 0.4% at 1000° A and 0.2% at 1500° A ; favouring in both cases the silica-rich phase.

OTHER PROCESSES LEADING TO ISOTOPIC FRACTIONATION

In the previous sections, we have worked out the maximum enrichment that can be expected from statistical exchange probabilities among silicates which have formed in equilibrium. There are, however, other conditions and other processes which under favourable circumstances may lead to isotopic separations, and the previous arguments have little significance of their own without considering these processes and weighing their possible influence on the problem in hand.

To begin with, it is usually assumed that no variations in isotopic abundances existed in the original magmatic material that formed—and is continuing to form—the solid crust; thus existing variations can be attributed to physical processes that have been operative within geological time, and not to incomplete mixing. As most theories of the earth's formation envisage a genesis from very hot gases,

the assumption is probably valid. Chemical fractionation would be infinitesimal at such high temperatures, and the turbulence that must have existed should ensure the complete mixing of the materials. Furthermore all of the evidence that has been published to date suggests that natural variations depend upon the geological history of the materials studied, and are not related to geographic location.

Laboratory methods of isotopic separation are well developed and understood, both in theory and practice. Natural processes are admittedly more complicated, because they generally involve complex mixtures of the laboratory methods, which in combination may be competitive and therefore not calculable by the ordinary laws of superposition. Furthermore, natural phenomena proceed under conditions of temperature and pressure which cannot be reproduced in the laboratory, nor are they limited by the shortness of time which prevails in all controlled experiments. Nevertheless, if we believe that geological phenomena are guided by ordinary physical laws of matter, then the "laboratory" methods—which are merely an analysis of nature—must constitute the basic ingredients of the natural processes and much can be adduced by studying their relevance to our problem.

There are both physical and chemical processes which may lead to isotopic separations. The former, which depend purely upon the physical properties of the materials, are essentially processes of diffusion; the latter, which depend upon the chemical properties, are essentially processes of preference or exchange. This paper has thus far been concerned with a particular case from the latter category; let us now consider the others.

I. Physical processes. In melts, diffusion may be brought about by (i) gravitational forces, (ii) temperature gradients, and (iii) gradients in osmotic pressures. Gravitational effects are reduced to insignificance by the enormous viscosities that exist in silicate melts, not to mention the possibility of convection currents. To give an example: The viscosity of the feldspars in the laboratory at 1200°C is of the order of 10^6 cgs units or higher† (EITEL, 1941). If free SiO_4 ions are allowed to diffuse through this fluid, those containing the heavier isotope should sink faster than the others, owing to their higher gravitational potential. We can use the Stokes formula to give an estimate of the relative velocity u :

$$6\pi\eta au = (m^* - m)g,$$

where a is the mean radius of the ion, assuming it to be spherical, and m is its mass. Admittedly, Stokes' formula was derived under the assumption that the viscous medium through which the spheres fall is continuous, and this certainly is no longer true when the spheres are molecules whose size is comparable with intermolecular distances within the fluid; thus a rigorous application of this line of reasoning would require the use of a correction term in the Stokes formula, but since we are only interested in orders of magnitude, there need not be any objection to omitting it. Putting $\eta = 10^6$ and $a = 1.5 \times 10^{-8}$ cm, and putting in the values of the other physical constants, it turns out that $u \cong 10^{-20}$ cm/sec; which means that if a number of isotopic SiO_4 ions were to begin at the same level, it would

† Orthoclase actually has a viscosity of 300×10^6 c.g.s. units at this temperature, and indications are that viscosities increase exponentially with pressure (DANE and BIRCH, 1938).

require over 5000 years for the heavier ones to attain an average separation from the others of one ionic diameter, due to gravity alone.

In melts containing two or more phases, a certain amount of diffusion of one substance through another is brought about through the gradients that inevitably exist in the osmotic pressures of the constituent phases. This process is amenable to a mathematical treatment, for it was adduced by FICK that the diffusing mass distributes itself with time according to the equation

$$D \frac{\partial^2 n}{\partial x^2} = - \frac{\partial n}{\partial t},$$

where n is the function that represents the number of molecules of a given species at a given time and place, and where D is the diffusion coefficient for the given species of molecule in a particular medium. This equation has a particular integral

$n(x, t) = \frac{n_0}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}$, which describes the distribution at time t of those molecules

which at $t = 0$ were concentrated in the vicinity of the plane $x = 0$. Therefore the probability that a single particle will lie between x and $x + dx$ after a time t is

$$p(x) dx = n(x, t) dx / \int_{-\infty}^{\infty} n(x, t) dx = \frac{1}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} dx, \quad (3)$$

and accordingly the mean square displacement of the particles in time t is

$$\int_{-\infty}^{\infty} x^2 p(x) dx = 2Dt.$$

The quantity $\sqrt{\Delta \bar{x}^2} = \sqrt{2Dt}$ is equal to the half-width of the probability distribution (3), and therefore it is an estimate of the distance of penetration of one substance by another in time t .

Silicate melts apparently have a tendency to break up into an orthosilicate and a parasilicate phase, the latter consisting of polymer networks of SiO_4 molecules and the former unlinked SiO_4 ions. Let us consider the diffusion of isotopic SiO_4 ions through a stable parasilicate melt, for it is difficult to imagine the inverse process taking place. The diffusion coefficient D for this system should be given to the correct order of magnitude by the Stokes-Einstein formula:

$$6\pi\eta aD = kT,$$

which gives a value of about $5 \times 10^{-13} \text{ cm}^2/\text{sec}$ at 1000°C . If D were to retain this value, the ions would be expected to move 1 cm on the average in about 3.2×10^4 years. Now the diffusion coefficient is related to the mobility of the ions by the Nernst-Einstein relation

$$D = ukT,$$

and all other things being the same, the mobility of an ion is approximately inversely proportional to the square root of its mass. Thus if D is the diffusion coefficient for the ordinary SiO_4 ion, that of the isotopic form of this ion at the same temperature will be $D^* \approx 0.979D$. Therefore, under the conditions described

above, it would require over a full minute for the two ions to achieve a mean separation of one diameter.

Another way of treating the question of diffusion, with a more realistic reference to mass spectrometry, is by dealing with concentrations rather than with molecular movements. If the concentration c_0 of a given type of molecule throughout the region $x < 0$ is initially uniform before migration begins, then its value at a later time may be found by superposing solutions of the type (3), and turns out to be

$$c(x, t) = c_0 \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right).$$

Isotopic abundance ratios S will therefore be represented by functions of the type

$$S = \frac{c^*}{c} = \frac{c_0^*}{c_0} \cdot \frac{\operatorname{erfc}\xi^*}{\operatorname{erfc}\xi},$$

where $\xi = \frac{x}{2\sqrt{Dt}}$ and $\xi^* = \frac{x}{2\sqrt{D^*t}}$. Now in general $\xi^*/\xi \approx \left(\frac{m^*}{m}\right)^{\frac{1}{2}}$, which will be very nearly unity, so that we may write $\xi^* = \xi + \Delta\xi$, and thus

$$\frac{S_0 - S}{S_0} \equiv \frac{\Delta S}{S_0} = \frac{2}{\sqrt{\pi}} \cdot \frac{e^{-\xi^2}}{\operatorname{erfc}\xi} \cdot \Delta\xi. \quad (4)$$

For the diffusion of isotopic SiO_4 ions $\xi^* = 1.0053\xi$. The highest accuracy that can be expected of mass spectrometers at present is about 0.25%. Thus equation (4) tells us that changes in the relative abundance of silicon isotopes due to diffusion becomes just perceptible to mass spectrometric analyses with a good instrument, when ξ is such that

$$G(\xi) = \operatorname{erfc}\xi - 4\pi^{-\frac{1}{2}} \cdot \xi \cdot e^{-\xi^2} = 0.$$

This function has only one zero, at $\xi = 0.32$. Therefore, the relation that is implied between x and t is

$$x = 0.64\sqrt{Dt}. \quad (5)$$

Thus at a distance of only 1 cm from the original boundary of the diffusing material, diffusion must proceed at 1000°C for at least 1.5×10^5 years before it produces a detectable effect on Si-isotopic ratios, while at a distance of 1 metre, the time required is about 1.5×10^9 years.†

When thermal gradients exist in a melt, a diffusion of matter takes place in which the lighter molecules migrate toward the warm wall and the heavier toward

† These times are, of course, directly proportional to the value of the viscosity of the melt. Thus if η were smaller than we have assumed, as might be the case, e.g., among basaltic melts, the critical time-distance parabola for the "threshold of observation" will be correspondingly less stringent; but in no event does it appear likely to invalidate the conclusion, set forth later, that the time of diffusion must be long in relation to the cooling-off period of the melt, in order for isotopic enrichment to become perceptible. The "minimum enrichment effect" to which these arguments relate, is that which occurs in the bulk concentration of silicon isotopes and not among the isotopes constituting the "diffusion front" which some authors deal with specifically. Diffusion fronts may have their uses, but when one deals, as in the present case, with one of the bulk constituents of the rocks, they would be impossible to detect.

the cold, the total effect being a redistribution in the concentrations of the materials present. This phenomenon was apparently first observed by LUDWIG and rediscovered later by SORET, who adduced at the same time that the magnitude of the effect was roughly inversely proportional to the temperature gradient. The physical mechanism is not yet sufficiently well understood to enable calculations of the coefficient of thermal diffusion to be made in terms of molecular constants, but it is possible to determine its approximate order of magnitude from the macroscopic form of FICK'S law.

When thermal diffusion has proceeded to the point where further separation is cancelled by the remixing effects of ordinary diffusion, an equilibrium concentration gradient is attained and the system is said to have reached a steady state. When this condition prevails, the time variation of the concentration function vanishes, and FICK'S law takes the form

$$D \frac{\partial c}{\partial x} = D_T \frac{\partial}{\partial x} \ln T \quad (6)$$

where D_T is the thermal diffusion coefficient. It is known that $D_T/D \propto cc^*$, where c and c^* are the fractional concentrations of the ordinary and isotopic molecules, respectively, and so we write $D_T = \alpha cc^*D$, where α is the thermal diffusion constant defined by CHAPMAN (1929) and is, to a first approximation at least, independent both of concentration and of temperature. Then if we assume $c^* \ll c$, the equation (6) has a solution

$$s = \frac{c^*}{c} \approx \beta T^{-\alpha}$$

so that

$$\frac{\Delta s}{s_0} = 1 - \left(\frac{T_0}{T} \right)^\alpha.$$

Experiments suggest that at least among weak solutions (FOURNIER, 1944) the constant α is given to a correct order of magnitude by the formula of WIRZ (1939)

$$\alpha = \frac{1}{9} \cdot \frac{\pi a^3 C_p}{c^* k}, \quad (7)$$

where C_p is the specific heat of the dissolved substance and k is Boltzmann's constant. In a highly viscous silicate melt, one might expect that the kinetic concepts that underlie the formula (7) will more or less break down, and as a result α will turn out to be smaller by many orders of magnitude than the formula of WIRTZ predicts. Even so, the WIRTZ value implies that a four-fold variation in

temperature is necessary in order to make $\frac{\Delta s}{s_0} = 0.0025$, and this state of affairs can

hardly be envisaged as persisting in any ordinary melt. Moreover, the time of "relaxation" that is required in order to establish the equilibrium concentration

gradient is of the order of $\frac{1}{\alpha D} \simeq 3 \times 10^9$ years.

There only remains the question of whether isotopic separation in melts can accumulate in any significant amount through the transport action of thermal convection currents in the neighbourhood of the hot or cold walls, according to the Clusius-Dickel mechanism. The transport function τ for the Clusius-Dickel separation column has been given as a differential equation by FURRY and JONES (1946):

$$\tau^* = Hcc^* - K \cdot \frac{\partial c^*}{\partial z}, \quad c^* \ll c \quad (8)$$

where H and K are functions of viscosity, temperature gradient and the dimensions of the system. General solutions of this equation for specified boundary conditions have been given by BARDEEN (1940), who considered the following three cases: a column closed at both ends, a column closed at one end, and a column closed at neither end. In each case, the solution for the separation factor c^*/c_0^* after a time t appears as the superposition of a steady state term and a series of transient terms which decay exponentially as t increases. The steady state term is in all cases

$$[c^*/c_0^*] = e^{AL},$$

where $A = H/K$ and where L is the total length of the column, and this function represents the maximum separation that is obtainable by the convection process. When the system consists of two plane walls, there is an optimum separation for which A takes a maximum value, which is

$$A_{\max} = \frac{\alpha}{21.8} \left(\frac{\Delta T}{T} \right)^{\frac{4}{3}} \cdot \left(\frac{\rho g}{\eta D} \right)^{\frac{1}{3}}. \quad (9)$$

The greatest value that $\frac{\Delta s}{s_0}$ can attain is

$$\left(\frac{\Delta s}{s_0} \right)_{\max} = 1 - e^{(A^* - A)L} = 1 - e^{AL} \cdot L\Delta A,$$

where $\Delta A = 0.007A$, and if we put this value at 0.0025, we have the relationship

$$ye^y = 142.5,$$

where $y = AL$. The root of this equation is $y = 3.66$, therefore from (7) and (9)

$$L \left(\frac{\Delta T}{T} \right)^{\frac{4}{3}} \cong 5 \times 10^5 \text{ cm.}$$

This means that, even if the temperature difference were of the same order of magnitude as the mean temperature of the melt, the column would have to have a total height of at least 5 km in order to produce a detectable variation in isotopic abundances by the Clusius-Dickel mechanism. For such a column, the "relaxation" time for transient effects is of the order of 2×10^{10} years.

Arguments of the type employed in this section can only give as answers the time required to produce a certain minimum effect. They cannot in themselves rule out the existence of the phenomena they describe, for clearly given enough

time, any amount of separation by diffusion is possible. The limiting factor in the case of melts is the time required to cool down to crystallization temperatures, and in the case of solids, the age of the mineral or, lacking such a detailed knowledge of geological conditions, the age of the earth's crust.

If a very extensive sheet of intrusive fluid whose thickness is $2L$ and temperature V penetrates into a medium at zero temperature† which has approximately the same thermal properties as the fluid and cools there by conduction, the temperature at the centre of the intrusive at a time t after emplacement is given by (cf. CARSLAW and JAEGER, §41)

$$\frac{v_c}{V} = \sum_{n=1}^{\infty} \frac{2L \exp(-k\beta_n^2 t/L^2)}{[\beta_n^2 + L + L^2] \cos \beta_n}$$

where β_n is the n^{th} positive root of $\beta \tan \beta = L$. When L is large, this becomes approximately,

$$\frac{v_c}{V} \cong \frac{4}{\pi} \sum_{n=0}^{\infty} (-)^n \frac{1}{2n+1} e^{-\frac{(2n+1)^2 \pi^2 kt}{4L^2}}, \cong \frac{4}{\pi} e^{-\frac{\pi^2 kt}{4L^2}}$$

since the series is very highly convergent. Therefore, assuming a diffusivity $k = 0.01$ c.g.s. units, which is about the average for igneous rocks, it follows that the time for the temperature at the centre of the intrusive to fall to $1/e$ of its initial value, is about $0.016L^2$ years, where L is in metres. If the thickness is 10 metres, the time is less than two years; if it is 1 km, the time is around 1.6×10^4 years.

It seems very unlikely therefore, on the basis of our present physical knowledge, that diffusion processes in magmatic melts contribute in any way to the creation of variations in natural abundances of the isotopes of silicon.

Diffusion in the solid state. In solid rocks, rates of ionic diffusion will be very much slower than in melts, but the time limitation is not nearly so severe, since in many cases the process may have been operative throughout a major portion of the earth's history. For ordinary diffusion through solid media, the coefficient of diffusion (cf. JOST, p. 142, 1951) is

$$D = nvde^{-(E+U)/RT} \quad (10)$$

where n is the number of particles per cc, z is the number of nearest neighbours of an interstitial vacancy, d is the distance between equivalent equilibrium positions in the lattice, v is the mean thermal velocity of the particles, E is the energy difference/mole between an interstitial site and a normal one, and U is the potential energy/mole separating the equilibrium position of a particle from its nearest interstitial vacancy.

There are indications that the diffusion coefficient for the silicate anions is not likely to be larger in order of magnitude than 10^{-26} cm² sec⁻¹, and equation (5) then tells us that at a distance $> 10^{-4}$ cm from the diffusing boundary, isotopic separations would not become perceptible until a time had elapsed that is at least as great as the age of the earth. Thus it is highly improbable that solid state diffusion plays any part in the geological separation of the isotopes of silicon.

† The temperatures are purely relative.

WIRTZ (1939) established that the thermal diffusion coefficient for the migration of normal lattice particles in ionic crystalline solids is related to the ordinary diffusion coefficient by means of the formula†

$$D_T = -cT \frac{\partial D}{\partial T} \quad (11)$$

By (10) and (11),

$$\alpha = \frac{E + U}{RT}, \quad \sim 2 \times 10^{-4},$$

using average values for the parameters v , d , n and z , and therefore a 10^6 -fold temperature gradient is required in order to produce the minimum detectable variation in isotopic abundances.

It seems doubtful, therefore, that thermal diffusion in the solid state contributes in any way to isotopic enrichment of silicon in rocks. It is true that SILVERMAN discovered positive evidence for the enrichment of the isotopic content of oxygen in rocks due to thermal diffusion, but this may have been due to the presence of the "free" oxygen in rocks which does not belong to the normal lattice structure, and therefore diffuses by a different mechanism from ionic migration.

II. Chemical Processes. Besides the equilibrium process of chemical exchange, the discussion of which has formed the main body of this paper, there are the dynamic chemical processes of solution and precipitation which might also be expected to affect isotopic ratios. The absence of crystal boundary effects upon the interchange of ions between solid silicates and solutions has been pointed out by MITRA and RAJAGOPALON (1948): consequently the tendency for ions to dissolve or to precipitate should be determined largely by their chemical potential. These processes are not yet amenable to rigorous theoretical treatment, but one may argue intuitively that inasmuch as the free energies of isotopic molecules are approximately inversely proportional to the square roots of their masses, the heavier isotopes should favour the undissolved or precipitated phase, and the lighter isotopes the dissolved phase, although in either case the preference is probably very slight. Therefore the continued action of weathering and leaching might be expected to enrich the undissolved particles in the heavy isotopes, while the material that is carried away in solution should be correspondingly impoverished. Similarly, material that is precipitated out of solution ought to possess a higher content of heavy isotopes than the liquid from which it precipitated, and so on. It is difficult to estimate the enrichment that may be obtained from any of these fractionating processes, but for a single stage it should be very slight. The effect, however, is unidirectional and it is therefore cumulative; and so continued recycling of erosion and sedimentation through geological ages may conceivably build it up to an amount that can easily be detected by the mass spectrometer.

One might also expect that a certain amount of chemical fractionation of isotopes may take place during the formation of a mineral, due to the dependence of bonding forces within lattice structures upon quantities which might conceivably be affected by the isotopic composition of the ions. Should this be true.

† The coefficient D_T is the one defined by CHAPMAN (1929). It is related to WIRTZ D' by $D_T = -cTD'$.

then the isotopic composition of minerals would show a marked dependence upon their chemical and crystalline structure that would be unaffected by their mode of origin, and this is known not to be the case. The existence of a single piece of contrary evidence is a condition both necessary and sufficient to reject this hypothesis.

Therefore, it seems that the chemical processes leading to variations in natural isotopic abundances in rocks are of two kinds: exchange processes proceeding under stable conditions in melts during the formation of minerals, and the fractionating processes of solution and precipitation. The former cannot produce variations that exceed a calculable figure, and evidently must cease with crystallization; the latter leads to effects that accumulate with time, and are limited only by the exposure of the material to the destructive forces of erosion.

SUMMARY

Small variations in the relative abundances of the naturally occurring isotopes of the elements are known to exist in nature, and in this paper we have discussed various mechanisms by which variations can come about, assuming that none existed before the crust began to form. Quantitative arguments deriving from the physical laws which underlie these mechanisms have been applied wherever possible to the case of silicon, and have enabled us to draw certain conclusions relating the distribution of the isotopes of silicon in a mineral to its geological background. Briefly, they are as follows:

1. In a suite of igneous rock types in their original state which have formed by sequential differentiation from a single matrix, the heavy isotopes should be found in greater abundance in the silica-rich phases than in the silica-poor ones, but in the case of silicon, the maximum variation between the two limits of the sequence should not exceed 0.5%. Therefore if the primordial abundance ratios are known (as found, for example, among young basalts), a limit may be set to the heavy isotopic content of rocks which have derived in their present form from an original magma.

2. Weathering and erosion tends to increase the proportion of heavy isotopes in rocks and undissolved grains; moreover, the effect is cumulative. Thus sedimentary material should have a higher heavy isotope content than the igneous rocks from which they derived, and the discrepancy should increase continuously with the degree of exposure. Therefore, since the enrichment process should continue as long as the material is subjected to the forces of erosion, it seems probable that after a certain amount of exposure the magnitude of the effect should surpass the variations due to chemical exchange. Precipitation from solutions is another cause of isotopic fractionation since the precipitates capture more than an equal share of heavy isotopes. Therefore an unusually high abundance of the heavy isotopes of silicon should be found in diatomaceous deposits, flints, and so on.

3. The fractionating effects of chemical exchanges fall off with increasing temperatures; therefore the isotopic fractionation due to these processes will be more marked among low temperature hydrothermal minerals such as quartz, opal, topaz, etc., than among the igneous rocks, reaching as much as 0.6%. Knowing

the average isotopic content of quartz, let us say, one can set limits to the compositions of other hydrothermal minerals within which the existence of reworking during their geological history is not a necessary hypothesis.

4. As a corollary to these conclusions, one may set up a sort of criterion or "scale" as follows: the lowest point shall correspond to the heavy isotopic abundance found among the youngest basalts, and the highest point to that found in diatomites. In between, the range is divided into the intervals appropriate to unaltered magmatic derivatives, hydrothermal residues, sedimentary deposits and precipitates, the limits corresponding to the hypothetical temperatures of formation. Such a scale might be used either (i) to suggest a rough magnitude for the temperature of formation of a mineral whose origin is known and which is known beyond a doubt to be substantially in an unaltered state, or (ii) in the case of minerals whose origin is in doubt, to determine whether or not it is necessary to assume exposure to reworking (erosion and sedimentation) during a part of their geological history.

This study was commenced while the author was a research associate of the Geophysics Laboratory at the University of Toronto, and completed when he was a visiting associate of the Department of Geodesy and Geophysics at the University of Cambridge. It is with pleasure that he acknowledges his gratitude to both of these institutions, and to the *Imperial Oil Company* of Canada, whose generous interest made possible his year of association with the University of Toronto.

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Book reviews

LYTTLETON, R. A: **The Comets and their Origin.** Cambridge University Press, 1953. 25s. net.

In this book the author gives an account of his new theory of the origin of the comets; the main part is rather technical, but since the author is of the opinion that the features of comets are not too well known even to astronomers, he begins by describing the dynamical and physical properties of comets as established by observational astronomy. These first two chapters of the book, which are enlivened by a great number of carefully chosen photographs of comets, can replace some of the earlier books on comets which appealed to a large circle of readers owing to the interest these unusual celestial objects arouse. The two subsequent chapters distinguish this book from all those previously written; here a new explanation for the origin and formation of comets and their tails is given which can claim to be a scientific theory, open to quantitative examination. The principal idea is briefly that the sun, during passages through galactic dust clouds, by its gravitational action causes the aggregation of dust particles; these clusters will revolve round the sun and, under favourable conditions, become visible to us as comets.

It will be for astronomers to test how far this new theory can explain all the strange observations made on comets throughout the centuries. It has the advantage of not introducing like most of the earlier comet theories new and unfounded hypotheses as for instance ejection of the cometary material from the sun or the planets, or pulverization of an asteroid. For the existence of dust clouds, on which the author's theory is based, there is ample evidence, and his views are also in full agreement with other recent cosmological theories which were developed without reference to the problem of comets.

One point may be of special interest to readers of this journal. Since SCHIAPARELLI's work we know that at least some periodic meteor swarms are genetically related to comets, and this assumption has sometimes been extended by astronomers to meteorites because it seemed simplest to consider meteors and meteorites as essentially the same celestial bodies, differing only in size. It is to the credit of geologists to have insisted that objects like meteorites can only have their origin in a celestial body akin to our earth, and not in a comet. Dr. LYTTLETON's inference that comets must be composed of small particles confirms this view. It is of course possible, and even likely, that some meteorites are so small that they are completely consumed during their flight through the terrestrial atmosphere and it may not be feasible, by watching the luminous effect in the sky, to distinguish them from meteors. But a meteor, of cometary origin, can never have the size, and even less the structure, of the meteorite specimens of our museums. If we make use of CHAMBERLIN's distinction between the "two solar families", planets and comets (and their relatives), then the meteors—at least those connected with comets—belong to the second family, but meteorites to the first.

F. A. PANETH

Gesteine und Minerallagerstätten, Band II, Exogene Gesteine und Minerallagerstätten by PAUL NIGGLI in collaboration with ERNST NIGGLI, Verlag Birkhäuser, Basel, 557 pp., 181 figs., 1952. Price (bound in linen) 49.40 Swiss francs, (in paper) 45.25 Swiss francs.

Volume II of *Gesteine und Minerallagerstätten* is a comprehensive treatment of the rocks of sedimentary origin and of the sedimentary ore deposits which they contain.

The book is divided into two parts: Part I concerns the autochthonous deposits and rocks formed by weathering and Part II treats the sediments. Each of these major divisions is subdivided into sections. Part I (117 pages) discusses weathering and soils. Part II (416 pages) covers A: Fragmental, clastic rocks; B: Pelite, gelite, humite, and related rocks; C: Carbonate rocks; D: Sedimentary phosphate deposits; E: Sulphate and chloride rocks and related salt deposits; F: Snow and ice; G: Petrographic provinces of sedimentary sequences. These sections are further subdivided into six subsections. Extensive bibliographies are given at the end of each subsection.

The NIGGLIS have made a detailed study of the sedimentary rocks from a quantitative standpoint. They have carefully analyzed a large amount of data, some of which was unorganized, and have presented their results in a unified form. The first part of this book presents the processes by which rocks are weathered, the chemical characteristics of the phases which are formed, and the chemical characteristics of the waters which aided in the processes.

The second part of the book is an analytical interpretation of the sedimentary rocks and of the means by which they originated. Much use is made of graphical interpretation of the chemical data on materials formed in similar geological environments. A large number of sedimentary-rock analyses, which have been gathered from widely disseminated sources, is included. NIGGLI symbols are given for many of the analyses.

Considerable stress is laid on physical and physico-chemical interpretations. Crystal-chemical concepts are used in the discussion of the minerals as phases in sedimentary rocks.

This work is an outstanding contribution to the mineralogy, petrology, and geochemistry of sedimentary materials.

GEORGE T. FAUST

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